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CHARACTERIZATION AND DEMULSIFICATION STUDIES ON OIL-IN-WATER EMULSIONS

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Coal Research Laboratory

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CHARACTERIZATION AND DEMULSIFICATION STUDIES ON OIL-IN-WATER EMULSIONS

by

S.P. Twa* and H.A. Hamza**

ABSTRACT

The results of the preliminary screening and testing of seven potential demulsifying chemicals supplied by Bayer A.G. Leverkusen (OBW 264244 - OBW264250) on an oil-in-water emulsion are described. Four of these chemicals produced clear oil and water separation with one of them BC-47, producing separation at a concentration as low as 100 ppm. Further tests with BC-47 showed that the best separation resulted when toluene was used as a solvent at a ratio of 2:1 toluene to oil, rather than at lower ratios. Toluene was also found to be a superior solvent to naptha. The demulsification process was found to produce better results when run at 60°C than when testing was done at 17°C.

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ÉTUDES PORTANT SUR LA CARACTÉRISATION ET LA DÉSÉMULSIFICATION DES ÉMULSIONS D'HUILE DANS L'EAU

par

S.P. Twa* et H.A. Hamza**

RÉSUMÉ

Le rapport porte sur les résultats préliminaires de l'étalonnage et du classement de sept produits chimiques, présentés par Bayer A.G. Leverkusen (OBW264244 - OBW264250), susceptibles d'être utilisés comme agents de désémulsification des émulsions d'huile dans l'eau. Quatre de ces produits chimiques ont permis une séparation nette de l'huile et de l'eau et avec l'un d'entre eux, le BC-47, la séparation s'est effectuée à une concentration aussi basse que 100 ppm. Des essais plus poussés à l'aide du BC-47 ont indiqué que la séparation la plus exacte se produisait quand on utilisait le toluène comme solvant dans un rapport toluène-huile de 2 à 1 plutôt que dans des rapports moins élevés. Le toluène s'est également avéré supérieur au naphta en tant que solvant. On a découvert que le processus de désémulsification donnait de meilleurs résultats quand il était effectué à une température de 60° C plutôt qu'à 17° C.

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INTRODUCTION

Bayer A.G. Leverkusen is involved in the manufacture of chemicals for potential use in separating oil (or bitumen) and water layers from oil-in-water emulsions. Previous work at the Coal Research Laboratory, Edmonton, has involved examining forty-three of these chemicals. This report contains the results of preliminary screening and testing of seven more potential demulsifying chemicals (OBW264244-OBW264250). Of these seven reagents (labelled BC-44 - BC-50), three (BC-46, BC-47 and BC-50) were found to be the most effective at various dosages in separating oil from water in an oil-in-water emulsion. BC-47 gave good separation over the widest range of the dosages tested and therefore most of the follow up testing was performed on BC-47.

Further testing using BC-46, BC-47 and BC-50 showed that toluene was a superior solvent to naphtha in improving the demulsification process. The greater the ratio of toluene to bitumen in the emulsion, the faster the separation and the lesser the degree of oil layer flocculation. BC-47 showed separation at all ratios of all solvents tested as well as with no solvent.

Tests performed at 17°C showed that BC-47 was not as effective at this temperature as at 60°C, which was the temperature used for the other demulsifier tests.

EXPERIMENTAL

In order to rate the effectiveness of the chemicals being tested the following criteria were considered:

- (a) the reagents that will effect a separation
- (b) the dosage of the reagent that will effect a separation
- (c) the time required for a separation to occur
- (d) the amount of water left in the separated oil (bitumen) layer and and the amount of oil left in the water layer (e.g. the clarity of the water layer)
- (e) the quality of the separated oil layer (e.g. flocculated or creamed)

A. Emulsion

The emulsion used for this work was an in-situ produced heavy oil (or bitumen)/water emulsion from the Fort McMurray, Alberta area and is a composite of a number of individual samples produced from different wells.

This emulsion was found to have a total bitumen content of 6.08% by weight as determined by gravimetric analysis (see Total Oil Analysis - Appendix A). The emulsion was tested with the Coulter Counter (particle size analyzer - see Appendix A) and was found to contain 4.17% particulates (bitumen) with a MESD (Median Equivalent Spherical Diameter) of 7.51 microns. The discrepancy between the total bitumen value of 6.08% and the Coulter Counter's 4.17% is mostly due to the prescreening that is necessary before running the emulsion sample on the Coulter Counter. This screening removes particulates larger than 38 microns which upon weighing were found to constitute 1.44% of the weight of the emulsion. Adding this value to that obtained from the Coulter Counter gives a total bitumen value of 5.61% which is close to the total bitumen value obtained gravimetrically (see Table 1). The water content of the emulsion was measured using a Mitsubushi Moisture Meter (see Appendix A) and was found to be 96.36%. The % bitumen and % water in the emulsion was checked periodically and was found to remain relatively constant over the testing period (see Table 2).

B. Demulsifier

The demulsifiers were prepared by diluting the received chemicals in deionized water to give solutions of 0.3% by weight of active solids. This was done by weighing the required amount of demulsifier into a 100ml beaker and then adding water to make up the solution to a total of 100g (see Table 3). The solutions were then stirred until complete dissolution was reached as judged by solution homogeneity. The chemical solutions used were freshly prepared each day.

C. Test Procedure

The demulsifier testing was done in 50ml capped glass culture tubes. Thirty ml of emulsion were pipetted into each tube. Since the prepared demulsifier solutions contained 0.3% active solids, addition of 1ml of this solution would correspond to a concentration of 100ppm with respect to the 30ml of emulsion. Since tests involved looking at the effect of up to

Table 1 - % Oil and Water Analysis of Stock Emulsion

<table>
<tr><th>METHOD</th><th colspan="2">% BITUMEN</th><th>% WATER</th></tr>
<tr><td>Coulter Counter (<38 μm)</td><td>4.17</td><td rowspan="2">5.61</td><td rowspan="2">*94.39</td></tr>
<tr><td>Oversize (>38 μm)</td><td>1.44</td></tr>
<tr><td>Gravimetric Analysis</td><td colspan="2">6.08</td><td>*93.92</td></tr>
</table>

*Calculated by difference from 100%

- See Figure 20 for the initial size distribution plot obtained from the Coulter Counter analysis of the stock emulsion.

Table 2 - Analyses of Stock Emulsion with Time

DATE	% BITUMEN (by CC,<38 μm)	% BITUMEN (>38 μm)	% BITUMEN (by G.A.)	MESD (from CC, μm)	% H_2O (by M.M.)
Sept. 13	4.17	1.44	6.08	7.51	96.36
Sept. 14	4.07	1.40	6.07	6.62	96.41
Sept. 22	3.02	-	5.11	5.63	95.22
Sept. 28	4.22	-	4.58	6.06	95.84
Oct. 04	4.45	-	4.89	6.06	96.31
Oct. 12	4.47	-	6.46	5.84	94.91

C.C. = Coulter Counter
G.A. = Gravimetric Analysis
M.M. = Moisture Meter

Table 3 - List of Chemicals Tested and Amounts Required of Each To Prepare Solutions Containing 0.3% Active Solids

EMR NO.	BAYER NO.	ACTIVE SOLIDS (%)	CHEMICAL ADDED (g)	WATER (g)
BC-44	OBW 2642/44	20	1.5	98.5
BC-45	OBW 2642/45	20	1.5	98.5
BC-46	OBW 2642/46	50	0.6	99.4
BC-47	OBW 2642/47	20	1.5	98.5
BC-48	OBW 2642/48	20	1.5	98.5
BC-49	OBW 2642/49	20	1.5	98.5
BC-50	OBW 2642/50	20	1.5	98.5
BC-17	OBW 2642/17	22	1.36	98.64

400ppm of demulsifier, up to 4 ml of solution were required. Therefore, in order to balance the total volume of reagents in the tubes containing less than 400ppm demulsifier, deionized water was added such that the combination of demulsifier solution and deionized water equalled 4ml (see Table 4).

The required amount of deionized water was therefore added to the emulsion and this is followed by a predetermined amount of solvent (usually toluene) which assists in solubilizing the bitumen in the emulsion. Finally the determined amount of demulsifier solution is added to give the desired dosage.

After all the reagents are added, the culture tubes were capped, placed in a support rack and inverted ten times to mix the contents. The tubes are then placed in a water bath (usually at 60°C) and a timer started. Photographs were taken of the tubes at specific time intervals starting at 15 seconds and ending at 24 hours.

D. Initial Screening

For comparison, the seven new chemicals (numbered BC-44 through BC-50) were tested by the same procedures as those followed for the other 43 Bayer chemicals previously tested (BC-1 to BC-43). Exact duplication of test conditions was not possible because the emulsion itself was different (i.e. 6.08% total bitumen content versus a 10.4% bitumen content for the emulsion used with the previously tested chemicals).

Prescreening of the chemicals involved testing their ability to effectively separate the oil and water within the emulsion at four different chemical concentrations (50, 100, 200 and 400ppm, based on the total volume of emulsion used). In addition, two blanks were included with each test for comparison purposes, one containing only emulsion, the other, emulsion, water and solvent (in amounts equivalent to that used in the reagent tests). Six samples in culture tubes were prepared and, after mixing, were photographed over 24 hours.

E. Solvent Optimization

A number of tests were carried out in order to determine the effect of the solvent to bitumen ratio on the performance of the demulsifiers. The solvents selected for these tests were toluene and naphtha. All previous work on the Bayer chemicals used toluene as the solvent. The volume ratio of

Table 4 - Volumes of Reagents Used in Initial Screening Test

CULTURE TUBE NO.	DEMULSIFIER DOSAGE(ppm)	EMULSION (ml)	TOLUENE (ml)	H_2O (ml)	REAGENT SOLUTION(ml)
1	0	30	3.0	-	-
2	0	30	3.0	4.0	-
3	50	30	3.0	3.5	0.5
4	100	30	3.0	3.0	1.0
5	200	30	3.0	2.0	2.0
6	400	30	3.0	-	4.0

toluene to bitumen used in testing BC-1 to BC-43 varied from about 4:3 for 0ppm of demulsifier to 2:3 for 400ppm of demulsifier (see previous report). In the initial screening of the seven new Bayer chemicals (BC-44 to BC-50), this ratio was kept constant at about two volumes toluene to one volume bitumen since previous emulsion work had shown this to be a suitable ratio. The solvent ratios examined in the solvent optimization test were 2:1, 1:1, 1:3, 1:5 and 1:10 for toluene and 2:1, 1:1 and 1:2 for naphtha. A few trials were also done without any solvent to determine the relative improvement in separation which resulted when solvents were used.

F. Temperature Effects

In previous tests on the intial 43 Bayer chemicals the optimum temperature for demulsification testing was found to be about 60°C. This is a preferable temperature because many of the emulsion samples were collected in the field at a wellhead temperature close to 60°C. The lower the reaction temperature at which a demulsifier works, the better the applicability in the field as this allows for fluctuations in the emulsion temperature without inhibiting the separation ability of the demulsifier. Therefore BC-47 was tested at a lower temperature (i.e. 17°C) to compare its performance with that which occurred at 60°C.

G. Concentration Optimization

It was hoped that the initial screening would identify some of the chemicals being tested as good demulsifiers for the emulsion being used. If this was the case a more accurate determination of the optimum demulsifier dosage could be determined by varying the chemical concentration more gradually (e.g. by 10ppm increments). In addition, the number of tubes used per test could be increased to cover a wider range.

RESULTS AND DISCUSSION

A. Initial Screening

In order to relate the new results (for BC-44 to BC-50) to previous ones (for BC-1 to BC-43), BC-17 was retested on the new emulsion. BC-17 in the previous test on the 10.4% oil-in-water emulsion showed oil and water separation starting at 50ppm and becoming much better at a 100ppm dosage.

The separation was most effective at 200ppm and declined at 400ppm (see previous report). On the present emulsion (6.08% oil-in-water), BC-17 showed separation starting at 50ppm (better than that noted previously) with the best separation occurring at 100ppm (see Figure 8). These results suggest that the lowest effective demulsifier concentration for BC-17 is dependent on the amount of bitumen present in the emulsion.

Of the seven new reagents (BC44-50) only four showed clear oil and water separation after 24 hours (see Tables 5 and 6 and Figures 1 to 7). The emulsion was effectively broken at 100, 200 and 400ppm for BC-47, at 200 and 400ppm for BC-46 and BC-50, and at 400ppm for BC-44. Table 7 shows the results of Coulter Counter and Moisture Meter analyses (see Appendix A) of samples showing good oil and water layer separation. The size distribution plots for these samples can be seen in Figures 21 to 32.

From the above results, most of the further testing was carried out using the best of these reagents which was clearly BC-47.

B. Solvent Optimization

The results shown in Figures 4,9,10,11,12 and 13 show that for BC-47 the separation starts faster at a 2:1 toluene:bitumen ratio than at lower ratios. For example, the separation starts at 15 sec. for 2:1 and at 30 sec. for 1:1. However, the separation with time following the initial period appears similar with lower solvent ratios such as 1:1 and 1:2 toluene:bitumen.

The separation in the cases of 2:1, 1:1 and 1:2 toluene:bitumen is significant at 100, 200 and 400ppm dosages of BC-47. At ratios of 1:3, 1:5 and 1:10 though, there was hardly any separation occurring at 100ppm. This is more likely due to the fact that tests using these lower toluene:bitumen ratios were run at a later date than the others and that the emulsion and/or the demulsifier had undergone some change (i.e. the % oil in the emulsion had changed- see Table 2). This is even more probable in light of the fact that tests run with no solvent, which were performed at the same time as the 2:1, 1:1 and 1:2 ratio tests, showed good separation at 100ppm.

Further observations on the results of tests using 1:3, 1:5 and 1:10 toluene:bitumen ratios show that at 200 and 400ppm BC-47 dosages, although the separation started at 30 sec., the rate and effectiveness of separation was not as good as that which occurred for the higher toluene

Table 5 - Approximate % Water Separated From Total % Water in Emulsion

REAGENT	CONCENTRATION (ppm)		
	100	200	400
BC-46	-	69	76
BC-47	80	86	88
BC-50	-	-	84
BC-17	86	87	-

Approximation made by volumetric measurement of clear water layer. A blank designates no clear separation observed.

Table 6 - Relative Degree of Flocculation and Water Clarity for Separated layers after 24 hours

CHEMICAL	50ppm	100ppm	200ppm	400ppm
BC-44	-	-	-	◔ XXX
BC-45	-	-	-	● XXX
BC-46	-	-	◔ XXX	⊕ XX
BC-47	-	⊕ XX	⊕ X	⊕ X
BC-48	-	-	-	● XXXX
BC-49	-	-	-	-
BC-50	-	-	◑ XXX	⊕ XX
BC-17	● XXX	⊕ XX	⊕ X	● XXXX

LEGEND:

Clarity
⊕ = Clear
◔ = Slight cloudiness
◑ = Cloudy
● = Milky or Opaque

Flocculation
X = None or very little
XX = Some Flocculation
XXX = More Flocculation
XXXX = All Flocculation

Table 7 - Analyses of Reagent Solutions Showing Good Separation

DEMULSIFIER AND DOSAGE LEVEL	WATER LAYER - BY C.C.		OIL LAYER - BY MM % H_2O *
	MESD (μm)	% OIL	
BC-44 at 400ppm	7.23	0.0077	70.5
BC-46 at 400ppm	6.68	0.0068	34.2
BC-46 at 200ppm	16.33	0.0221	94.0
BC-47 at 400ppm	11.12	0.0032	0.027
BC-47 at 200ppm	6.42	0.0022	0.11
BC-47 at 100ppm	13.26	0.0078	60.7
BC-48 at 400ppm	5.36	0.1103	72.0
BC-50 at 400ppm	8.90	0.0051	0.66
BC-50 at 200ppm	5.50	0.0922	74.2
BC-17 at 400ppm	5.00	0.0018	0.22
BC-17 at 200ppm	17.10	0.0031	0.06
BC-17 at 100ppm	4.55	0.0066	57.7

CC = Coulter Counter
MM = Moisture Meter
*High percentages suggest high degree of flocculation

ratio tests. This is observed in the lower toluene ratio tests by a greater degree of flocculation and by the presence of a flocculated portion of the oil layer which remains in the lower portion of the culture tube. This lower portion increases in volume and takes longer to rise and join with the upper floating oil layer as the ratio of solvent decreases. After 24 hours, the floating oil layers for the 1:3, 1:5 and 1:10 tests were more flocculated than those for the higher toluene ratios. Thus, in those tests solvent appears to promote oil layer flotation and creaming.

Figures 14, 15 and 16 illustrate the results for the tests using naphtha. The trend for the separation is similar to that for toluene i.e. the separation started earlier for a 2:1 ratio than for 1:1 and 1:2 ratios although the separation at later times appears to be equally good for all three ratios. The tests using naphtha also showed longer layer separation times than those for toluene, having larger portions of the oil layer remaining at the bottom of the culture tubes for longer periods of time. However, after 24 hours, the volumes of the oil layers were similar for both the toluene and naphtha tests with the only real difference being that there was more oil sticking to the sides of the glass tubes in the cases where naphtha was used.

The effect of BC-47 was also investigated in the absence of solvent as seen in Figure 17. The photographs show that though the separation was quite good and similar in effectiveness to the cases where solvent was used, the oil layer tended to remain on the bottom of the culture tubes for longer periods. In fact, in the final 24 hour photograph, the bulk of the oil layer in the 200ppm tube was still sitting on the bottom. The upper oil layer was in less of a flocculated state than the lower portion and in this case had a tar-like consistency, and these characteristics were also obvious in cases where very little solvent had been used.

For further demulsifier testing it was decided to use toluene as the solvent and to continue using it in a ratio of 2:1 toluene to bitumen by volume.

C. Temperature Effects

The results shown in Figure 18 indicate that while BC-47 was a good demulsifier at the lower temperature, the oil and water layer separation took longer at 17°C and the oil layer was much more flocculated after 24 hours than at 60°C (see Figure 4). These results support the previous work which shows that the higher the reaction temperature, the better the separation.

D. Concentration Optimization

From the initial screening tests on BC-47 it was shown that the lowest effective demulsifier dosage was 100ppm. In order to determine the optimum demulsifer dosage more accurately, experiments were run in which the concentration of demulsifier was varied more gradually. The first of these tests examined concentrations mainly between 50 and 100ppm and varying by 10ppm increments. The results, however, showed not as clear a layer separation at 100 ppm as had been previously observed. It is important to note that the emulsion's characteristics (i.e. % bitumen) were gradually changing so complete reproducibility was not always possible. The second experiment therefore looked at concentrations mainly between 100 and 200ppm. The results for this test (see Figure 19) showed clear layer separation between 100 and 110ppm.

From the results it can be concluded that BC-47 is an effective demulsifier on the emulsion tested at close to 100ppm and remains effective to at least 400ppm. This wide range of usability makes BC-47 potentially a very useful industrial demulsifier. BC-17, which is also a good demulsifier, doesn't appear to be as effective as BC-47 at higher concentrations (i.e. 400ppm) because of the reduced clarity of the water layer.

CONCLUSIONS

Of the seven new chemicals tested BC-47 was found to be the best. It caused oil and water separation at the lowest dosage and had a very wide range of effectiveness (from about 100 to at least 400ppm, which was the highest dosage tested). BC-46 and BC-50 were also effective demulsifiers showing good separation but only at dosages closer to or greater than 200ppm.

BC-17 was found to be the best of the previously tested 43 Bayer chemicals and although it gave oil and water layer separation at a lower dosage (near 50ppm) when tested against BC-47, BC-17 did not give as high a clarity water layer over as wide a range of concentrations as BC-47 did. Therefore, at least in industrial applications, BC-47 appears to be the more promising demulsifier.

Results from the solvent tests indicate that using toluene as a solvent gives faster separation times than if naphtha or no solvent at all is used. Additionally, the highest toluene:bitumen ratio tested (2:1 by volume) also gave faster separation times than the lower toluene:bitumen ratios.

Separation was observed to occur at a faster rate for a test run at 60°C than for one run at 17°C.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the work of I. McIver (University of Victoria) who assisted with the experimental work in this report during a co-op work term (September - December 1982).

FIGURES

#1 to #32

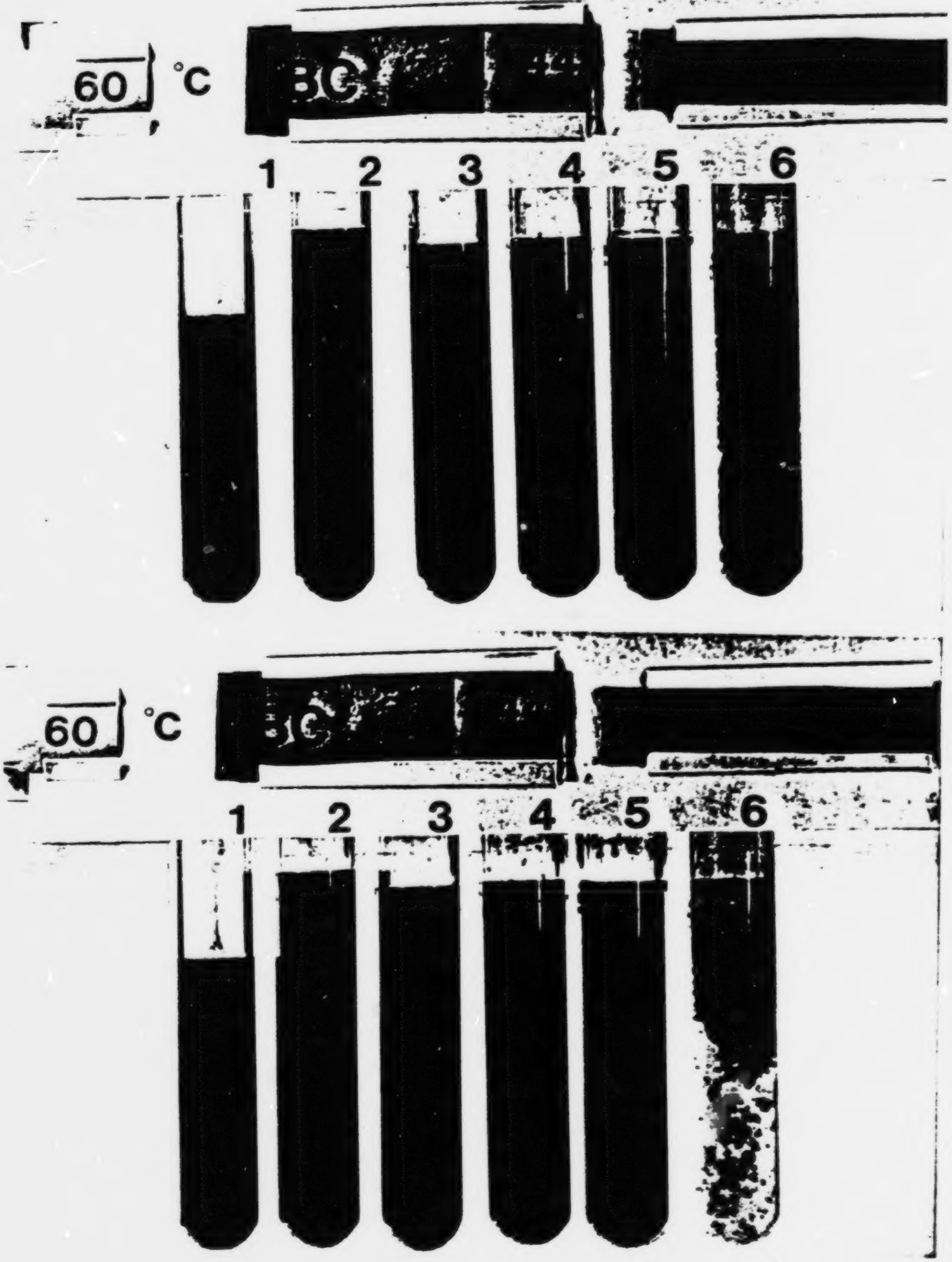
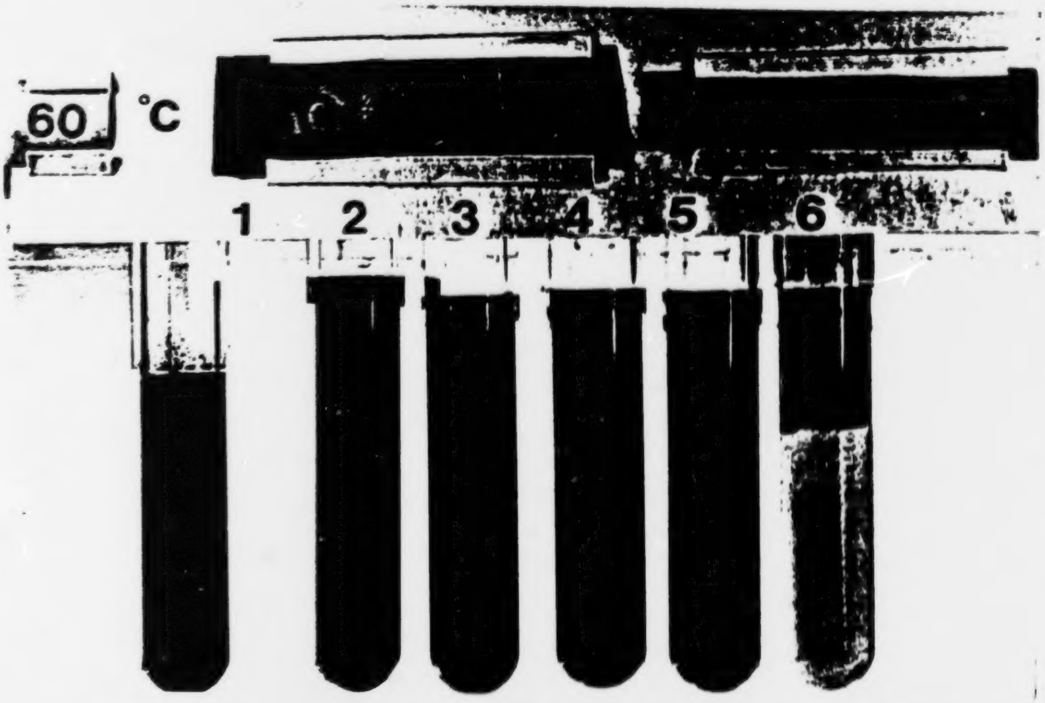

60 °C
BC 44
1
2
3
4
5
6
60 °C
BC
1
2
3
4
5
6

Figure 1: Initial screening BC-44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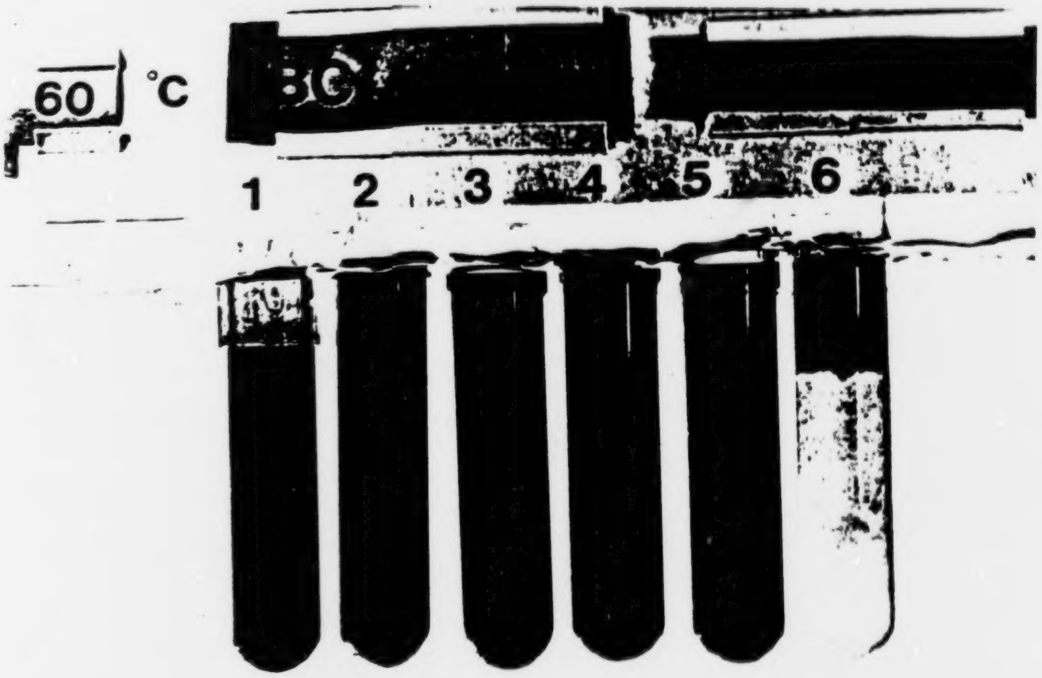
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BC
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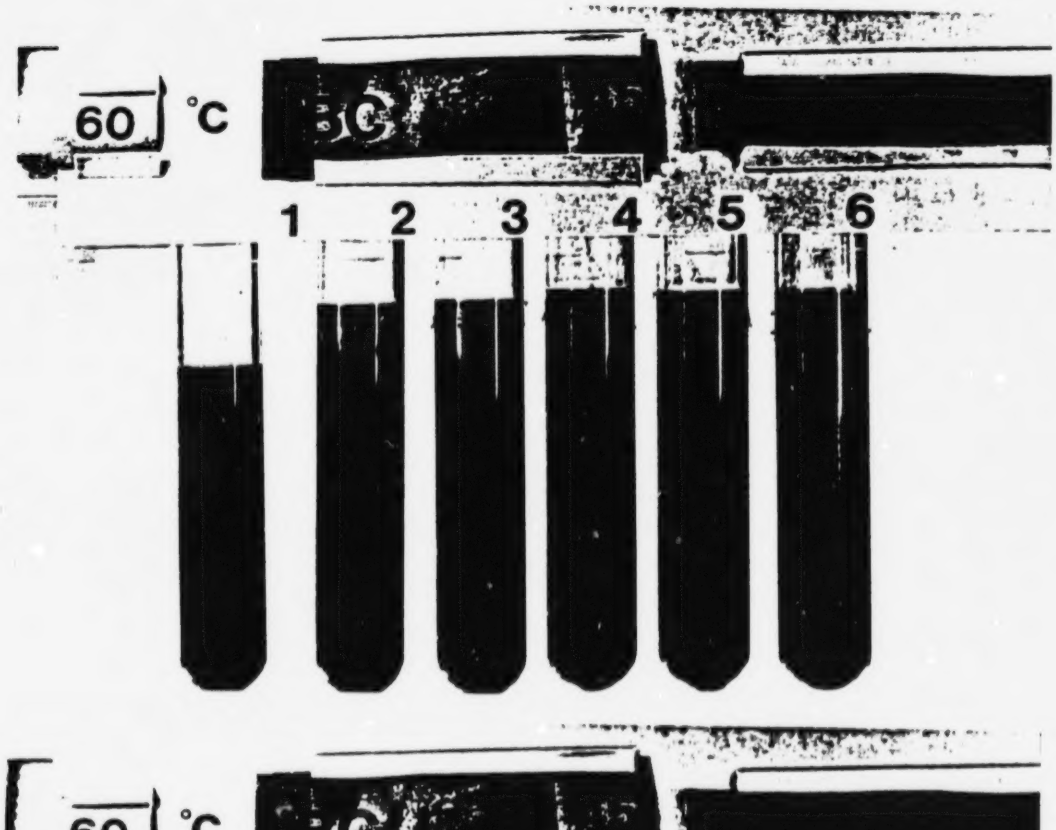
6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60 °C
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2
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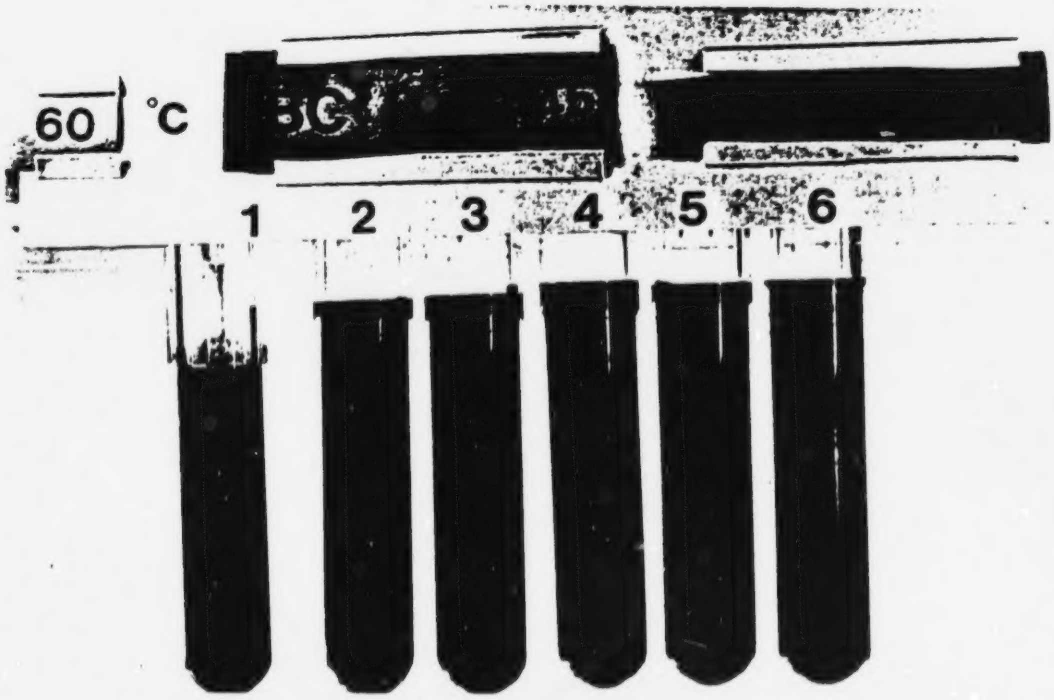
6

Figure 2: Initial screening BC-45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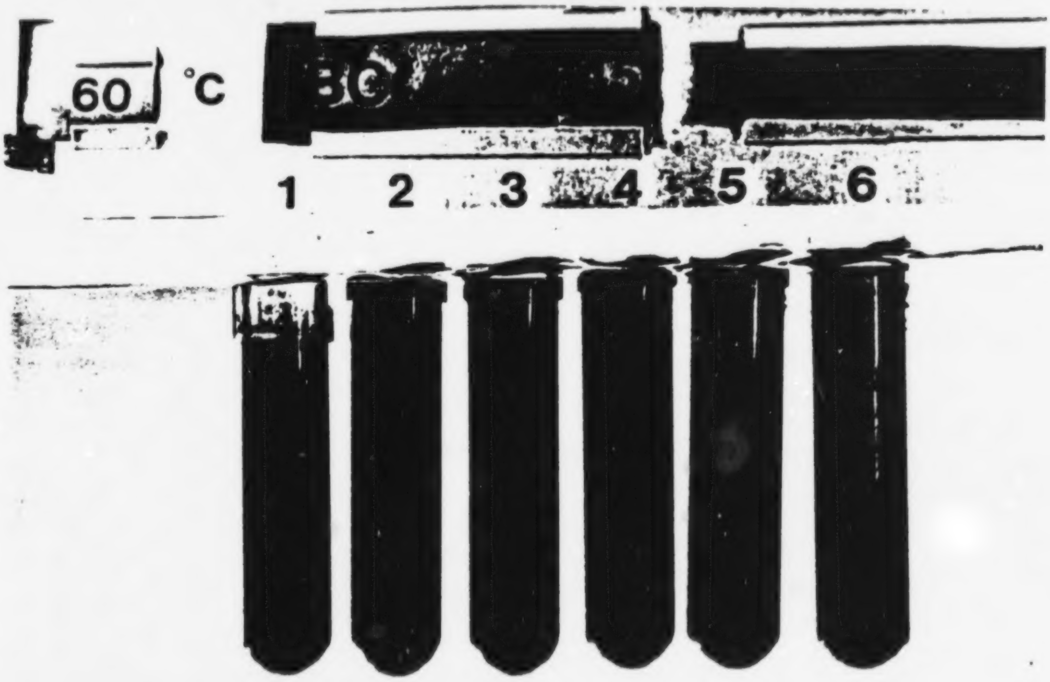
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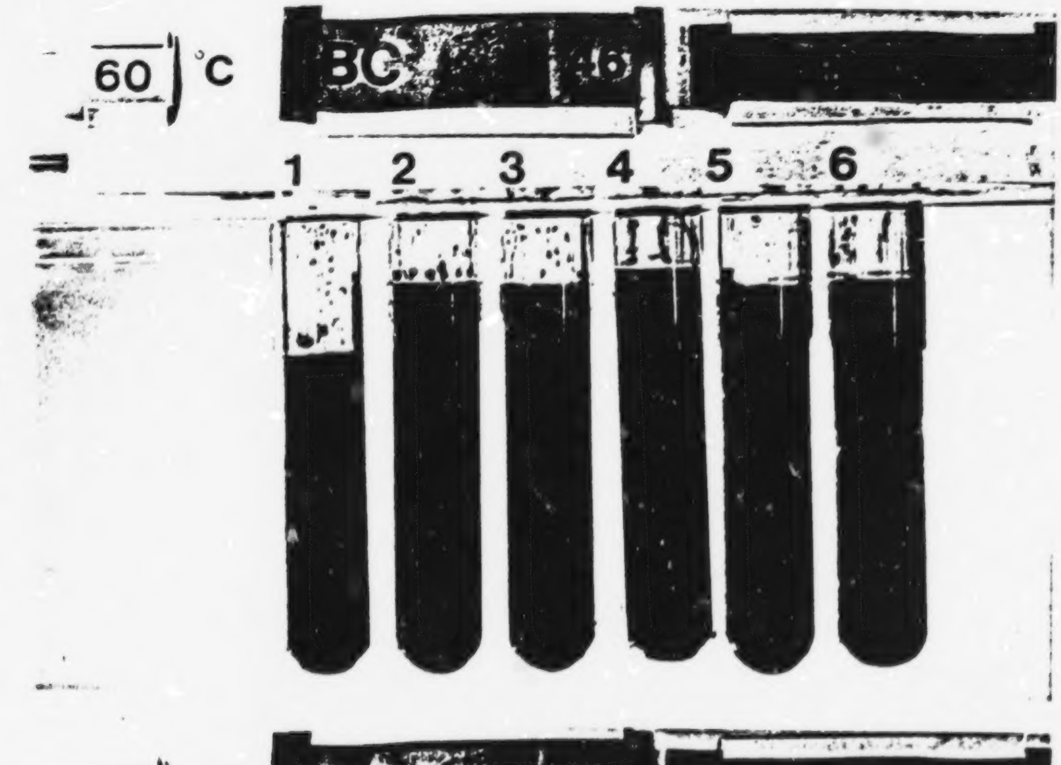
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BC 46
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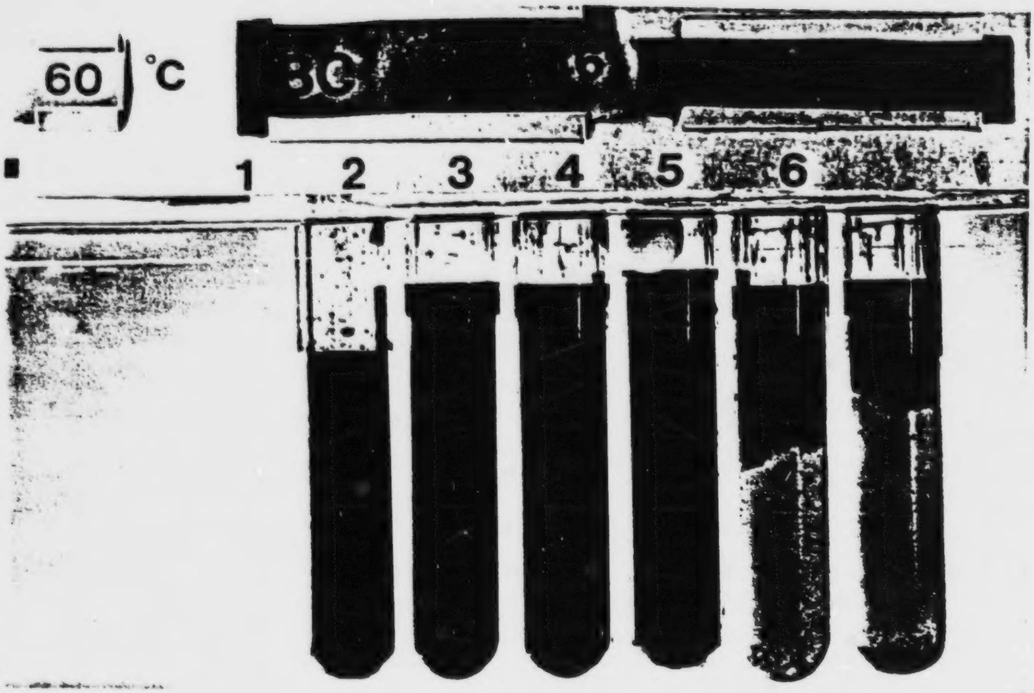
2
3
4
5
6
60 °C
BC 46
1
2
3
4
5
6

Figure 3: Initial screening BC-46


60 °C
1
2
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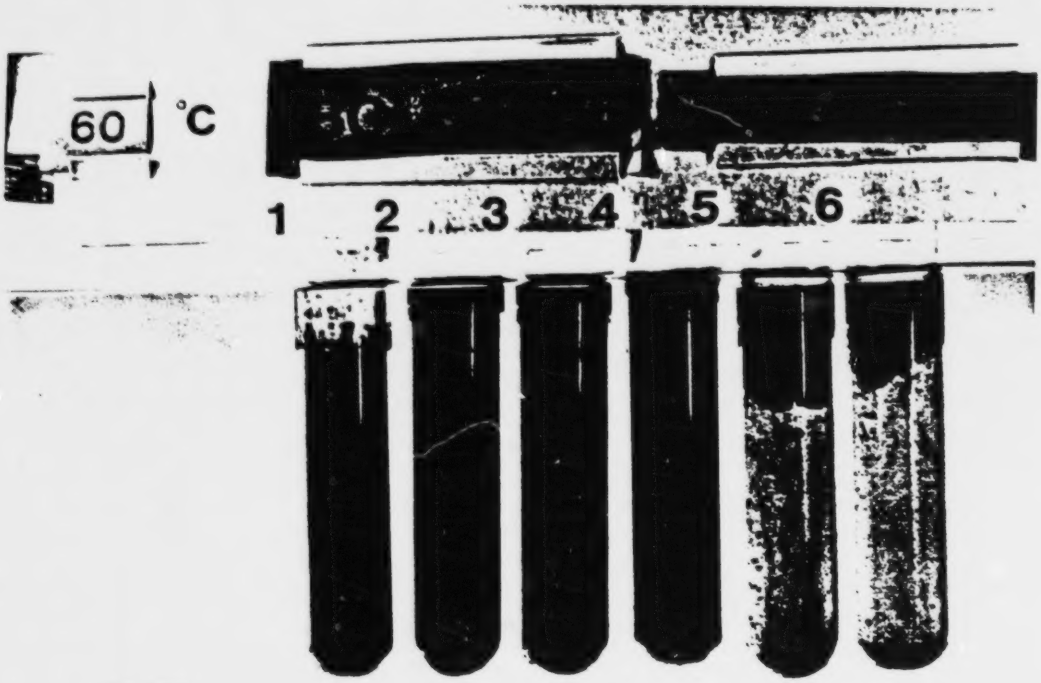
5
6


60 °C
1
2
3
4
5
6

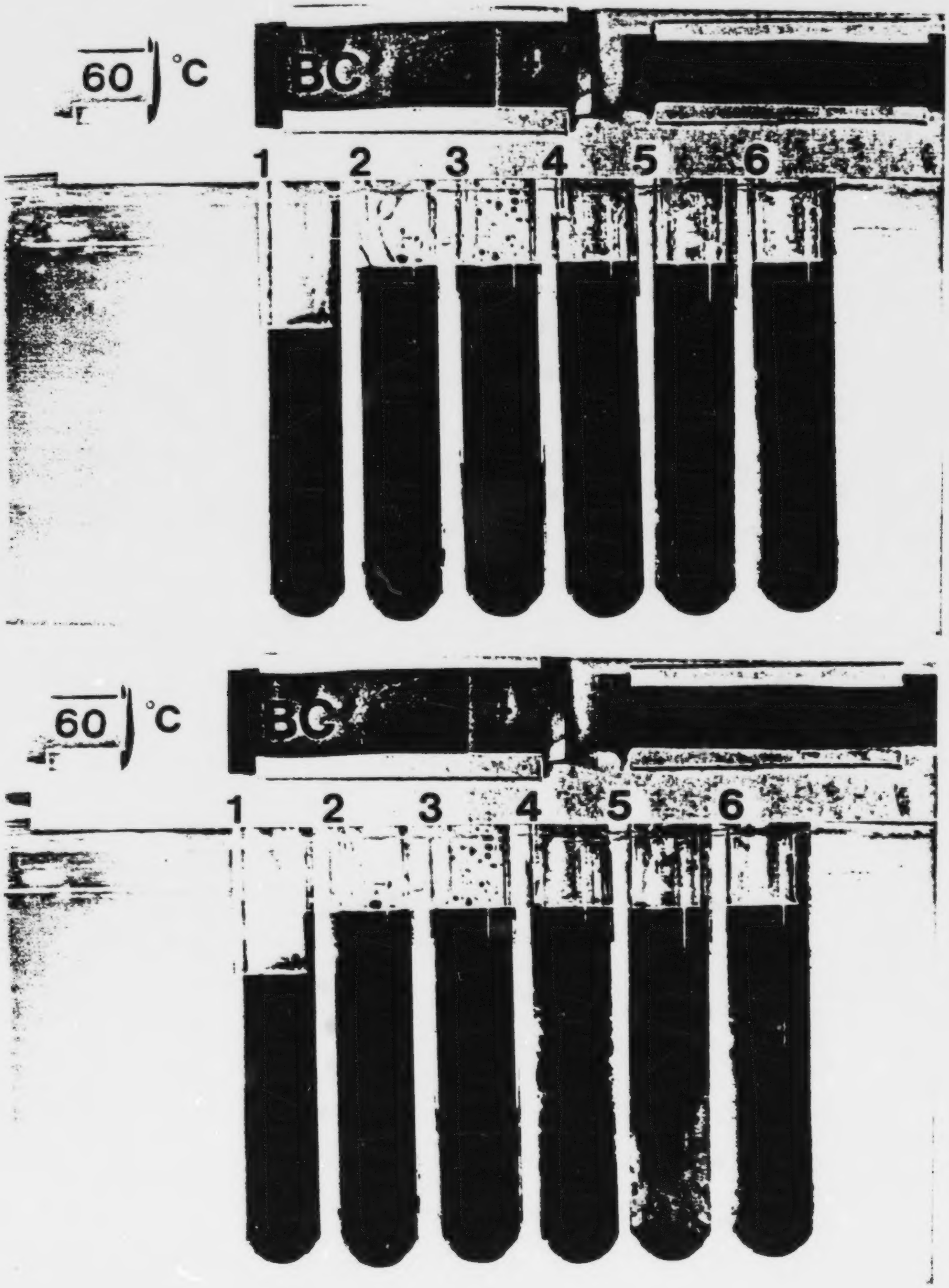
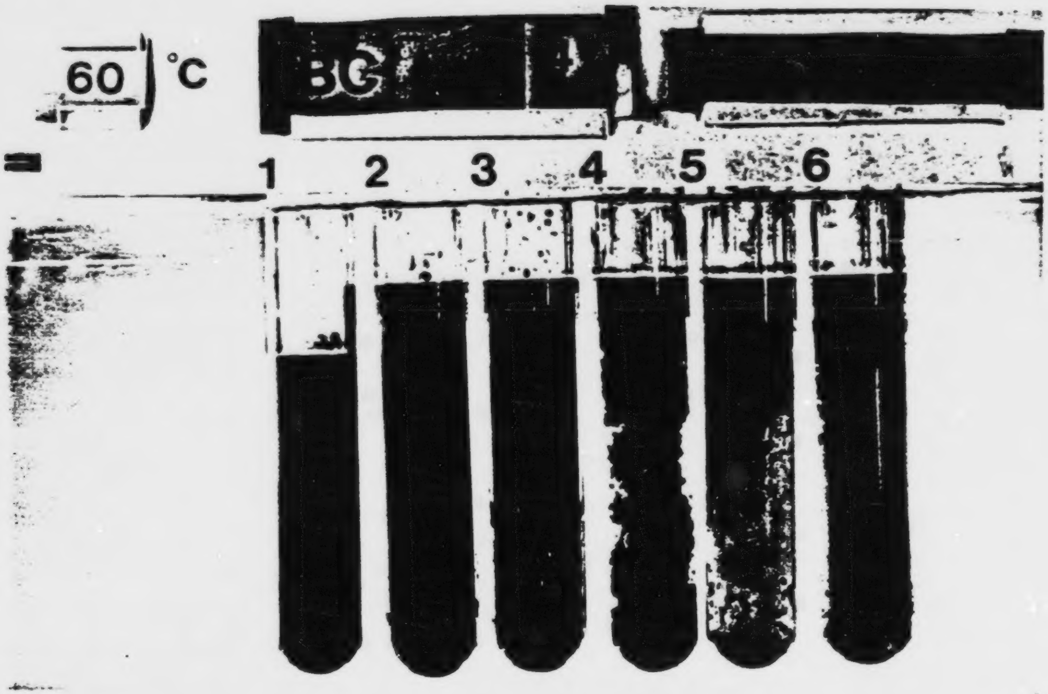
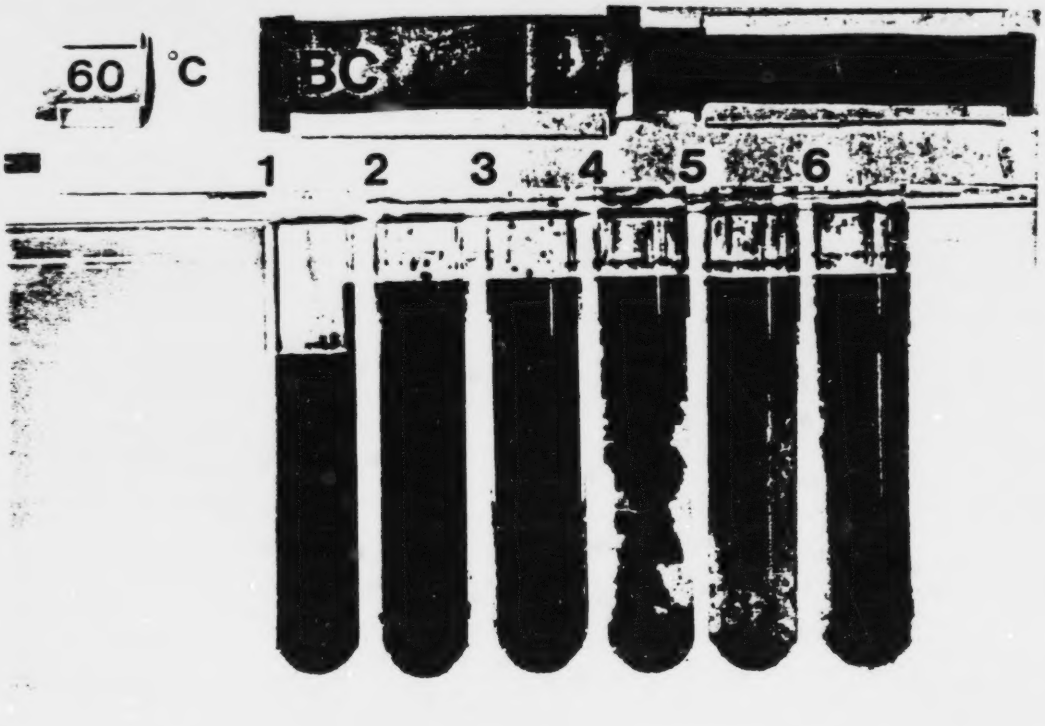

60 °C
BC
1
2
3
4
5
6
60 °C
BC
1
2
3
4
5
6

Figure 4: Initial screening BC-47


60 °C
BC
1
2
3
4
5
6


60 °C
BC
1
2
3
4
5
6

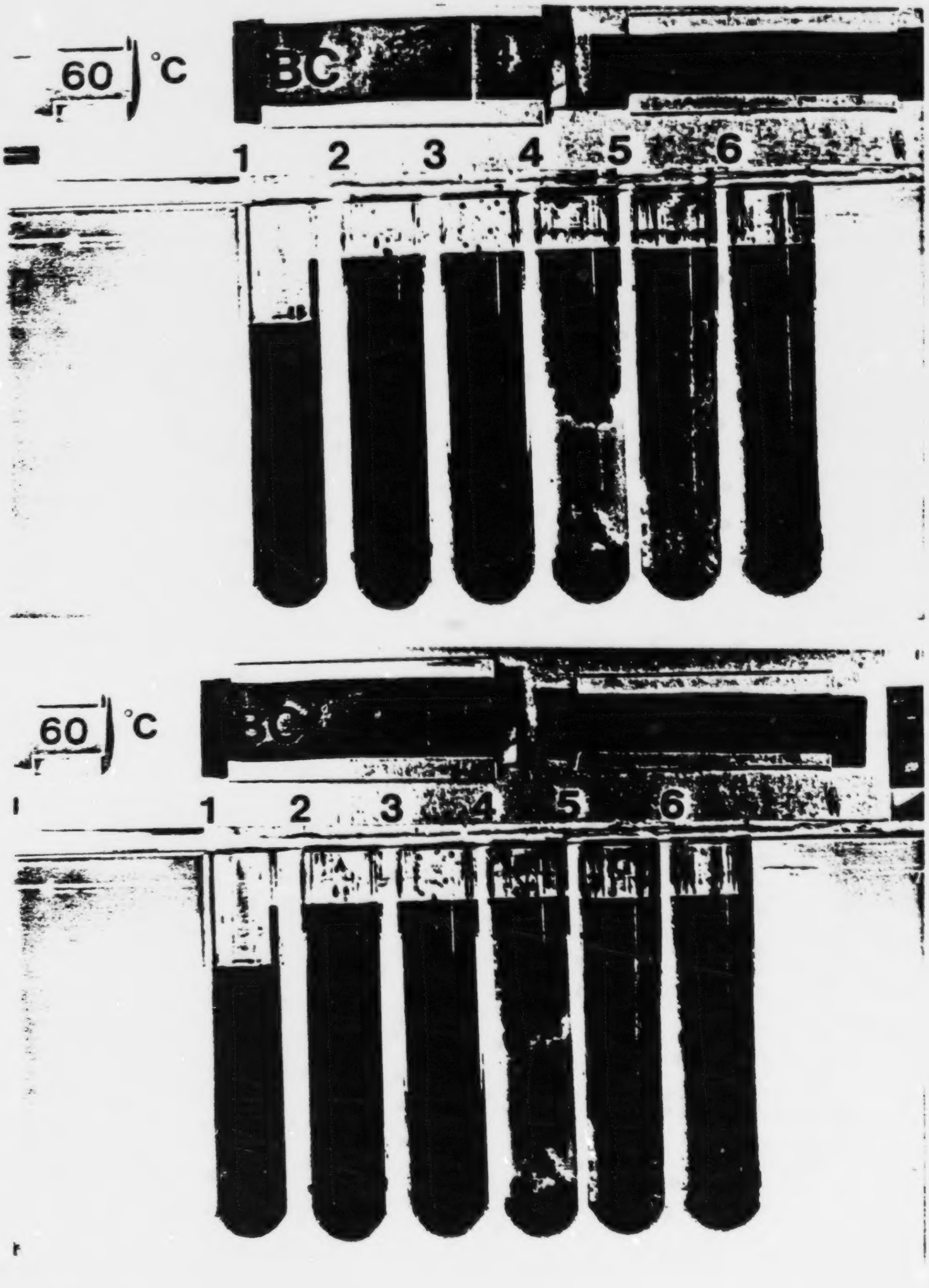
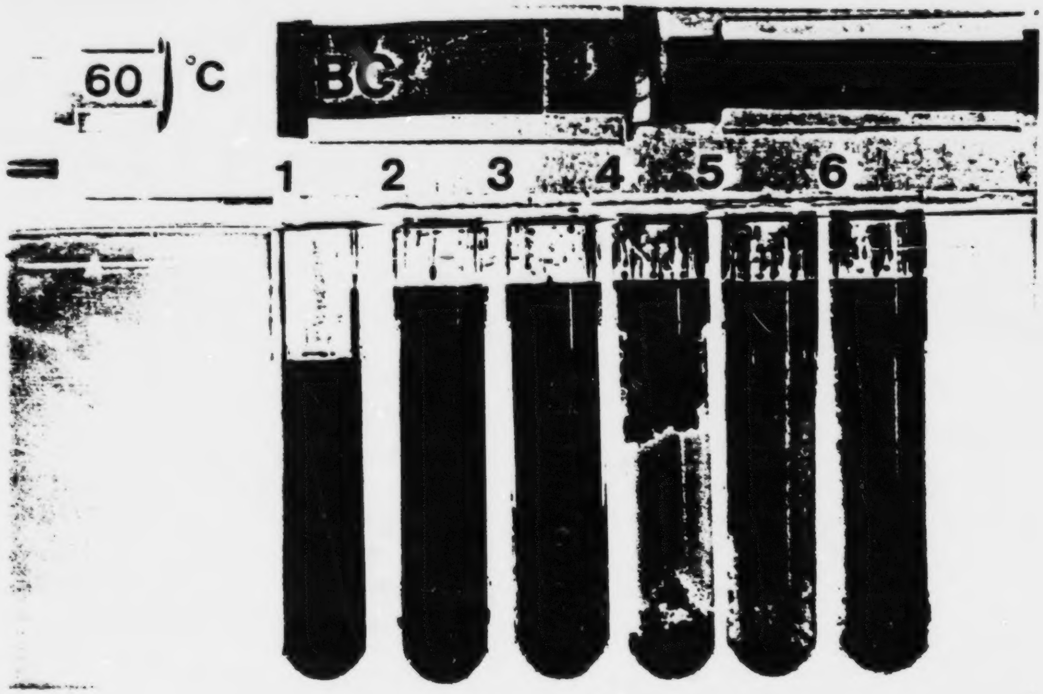
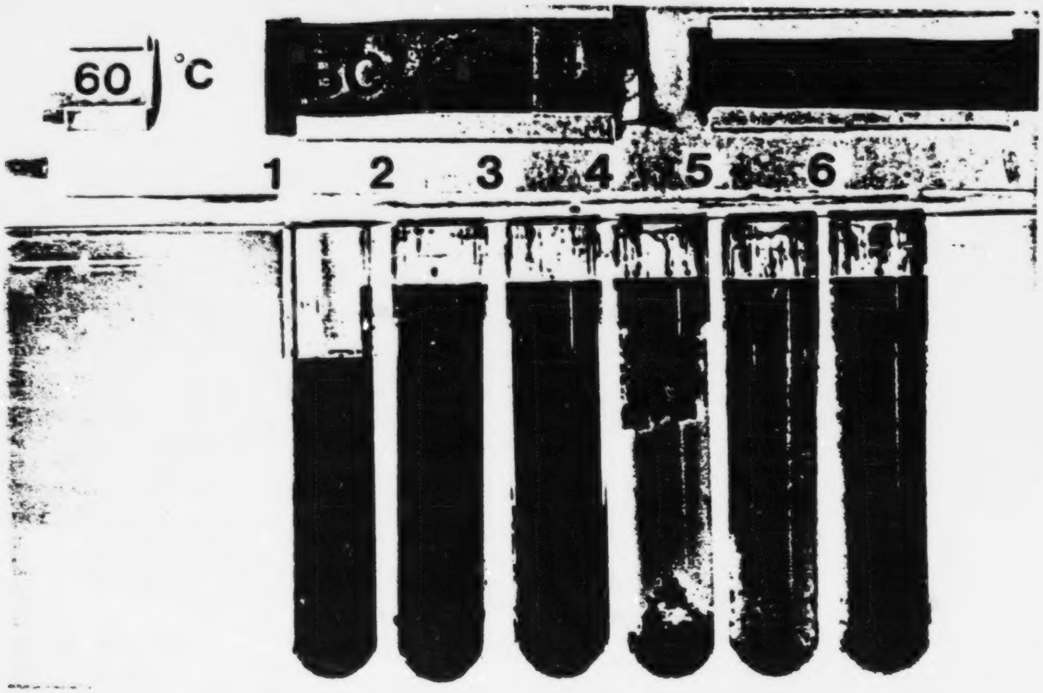

60 °C
BC
1
2
3
4
5
6

Figure 4 continued


60 °C
BC
1
2
3
4
5
6


60 °C
BC
1
2
3
4
5
6

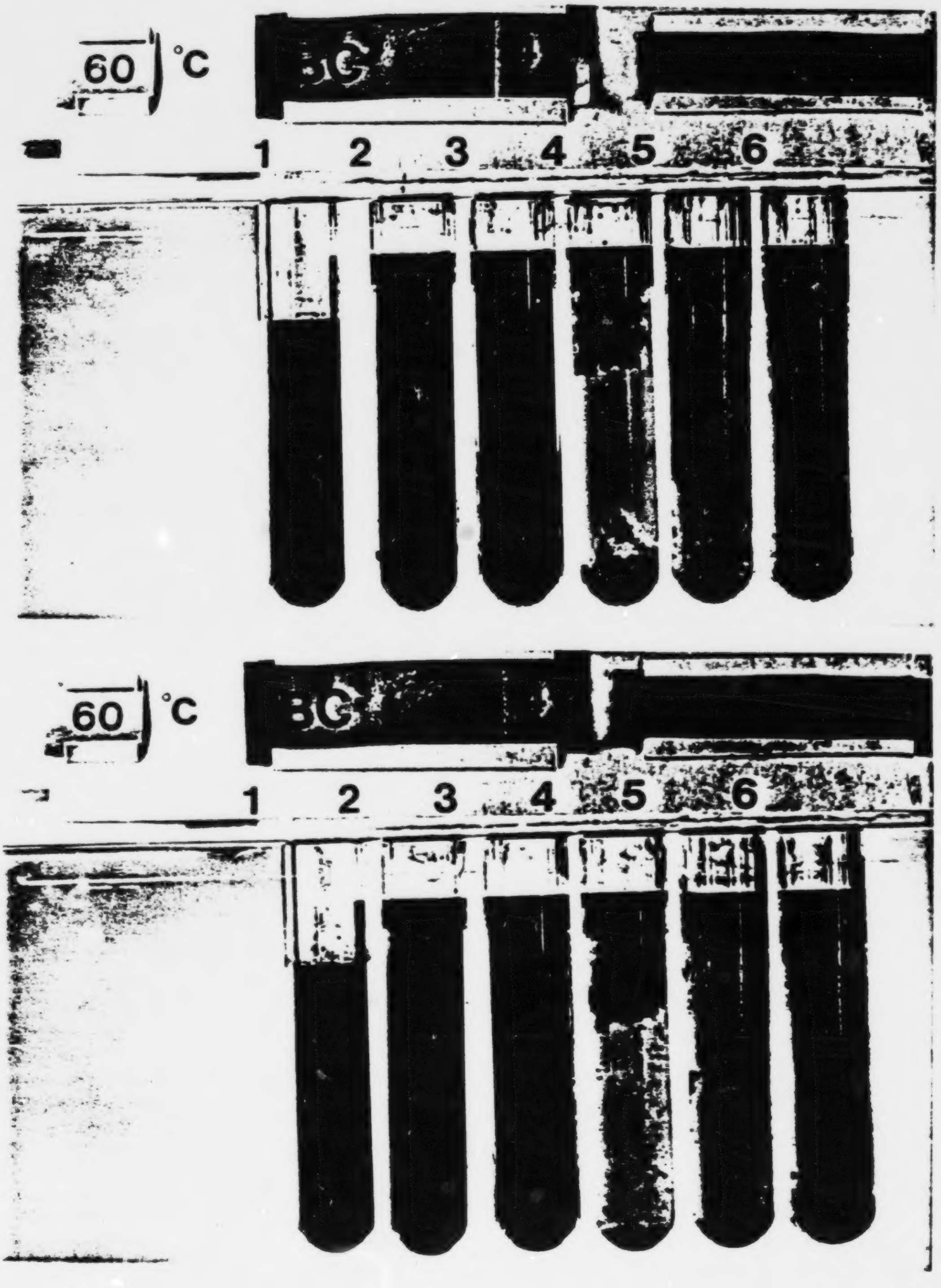
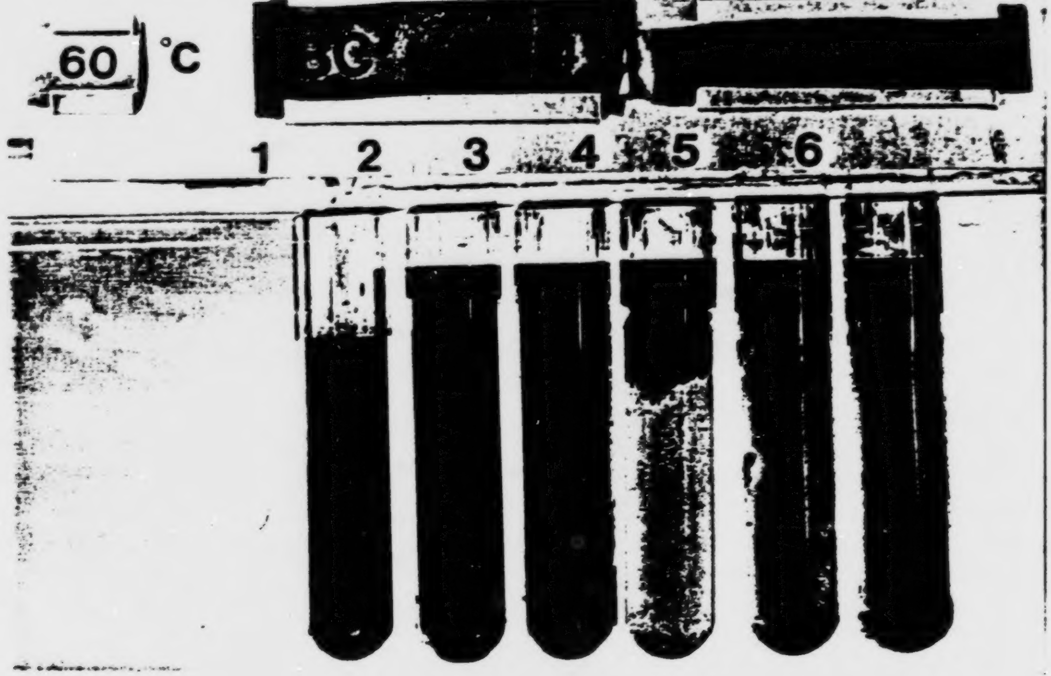
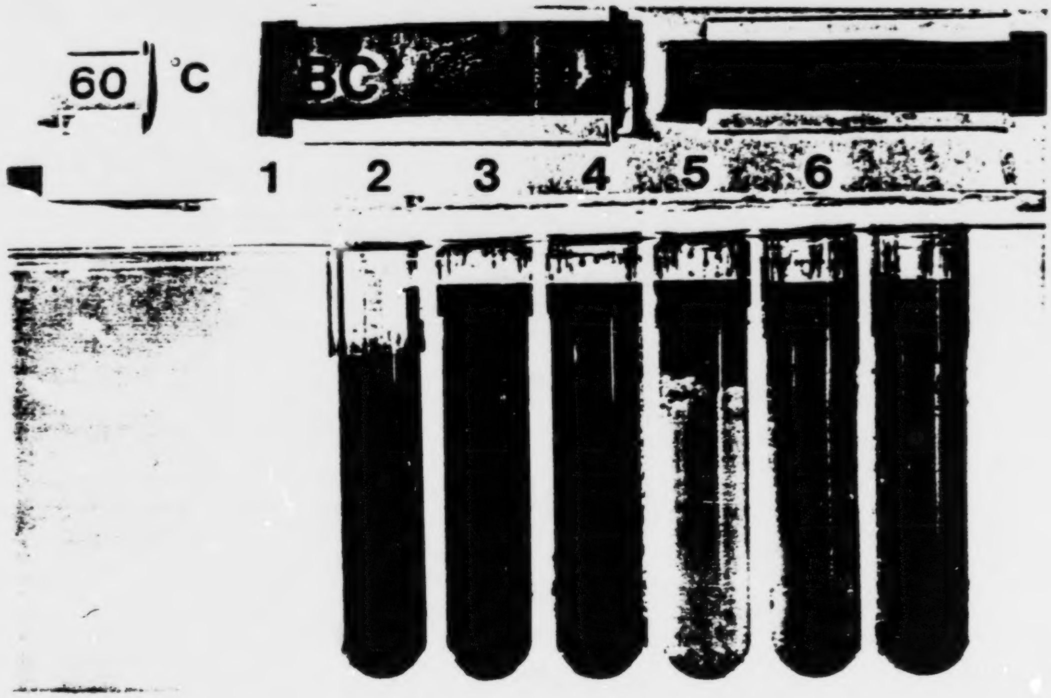

60 °C
BG
1
2
3
4
5
6
60 °C
BG
1
2
3
4
5
6

Figure 4 continued


60 °C
BC
1
2
3
4
5
6


60 °C
BC
1
2
3
4
5
6

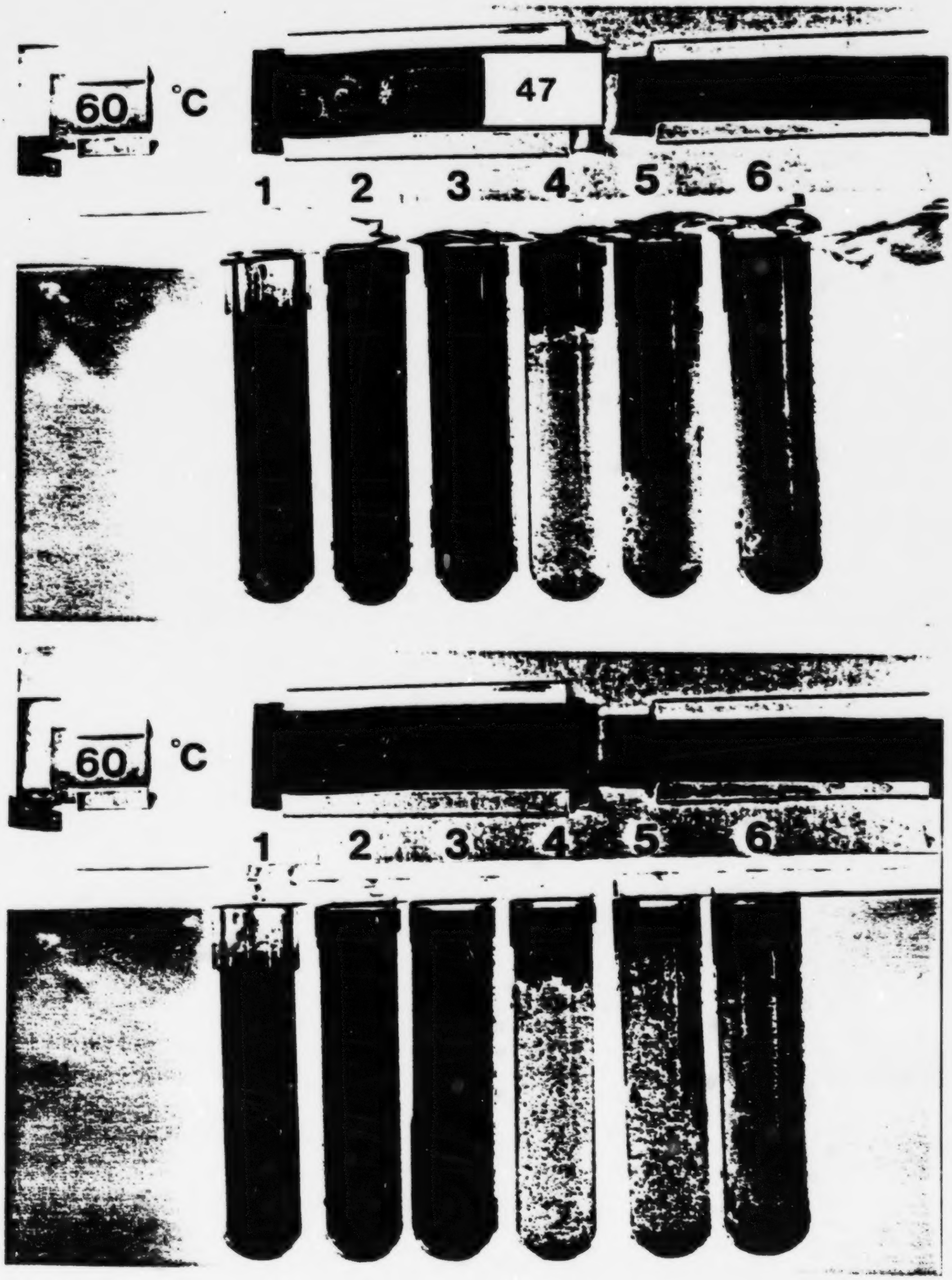

60 °C
47
1
2
3
4
5
6
60 °C
1
2
3
4
5
6

Figure 4 continued

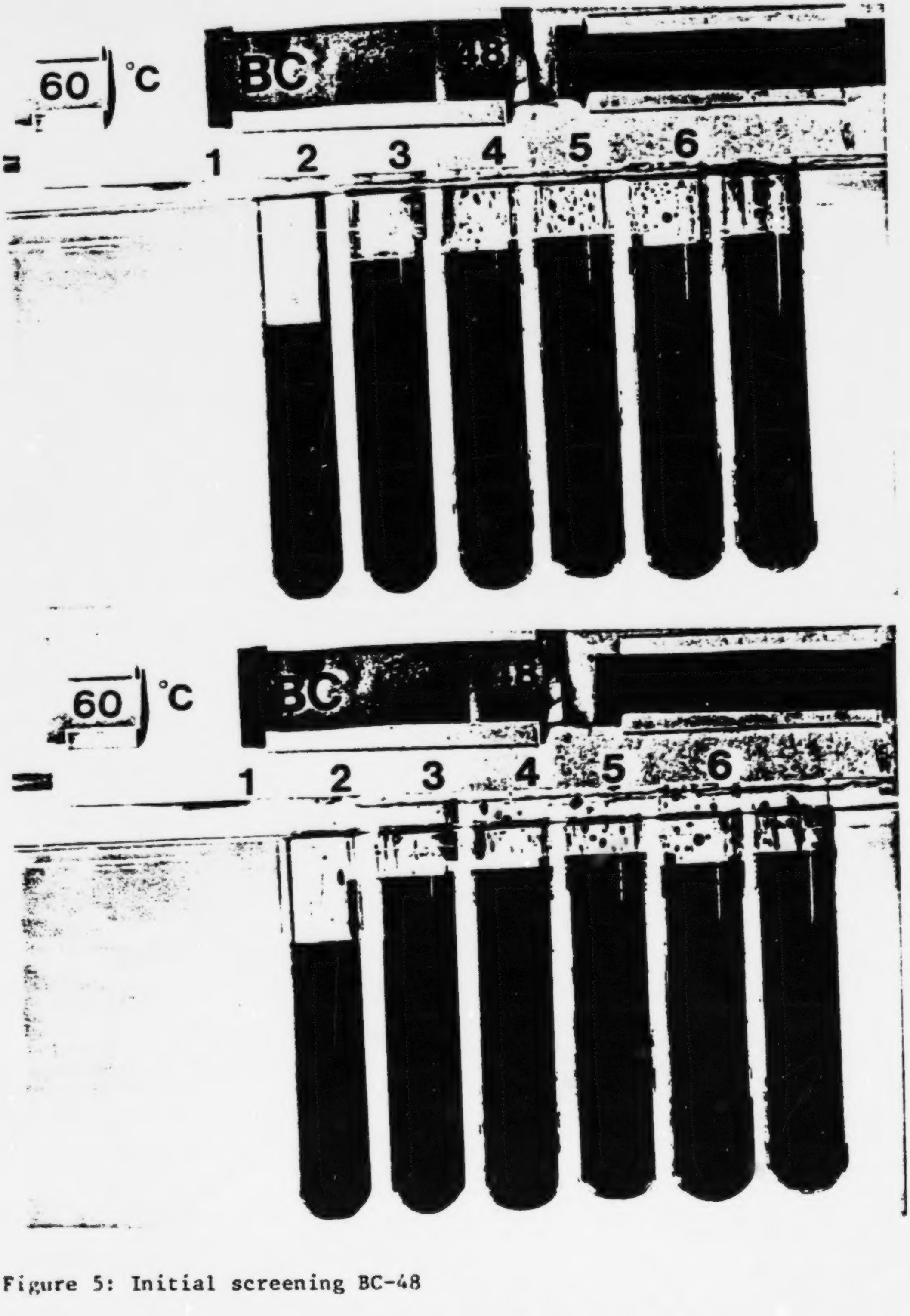
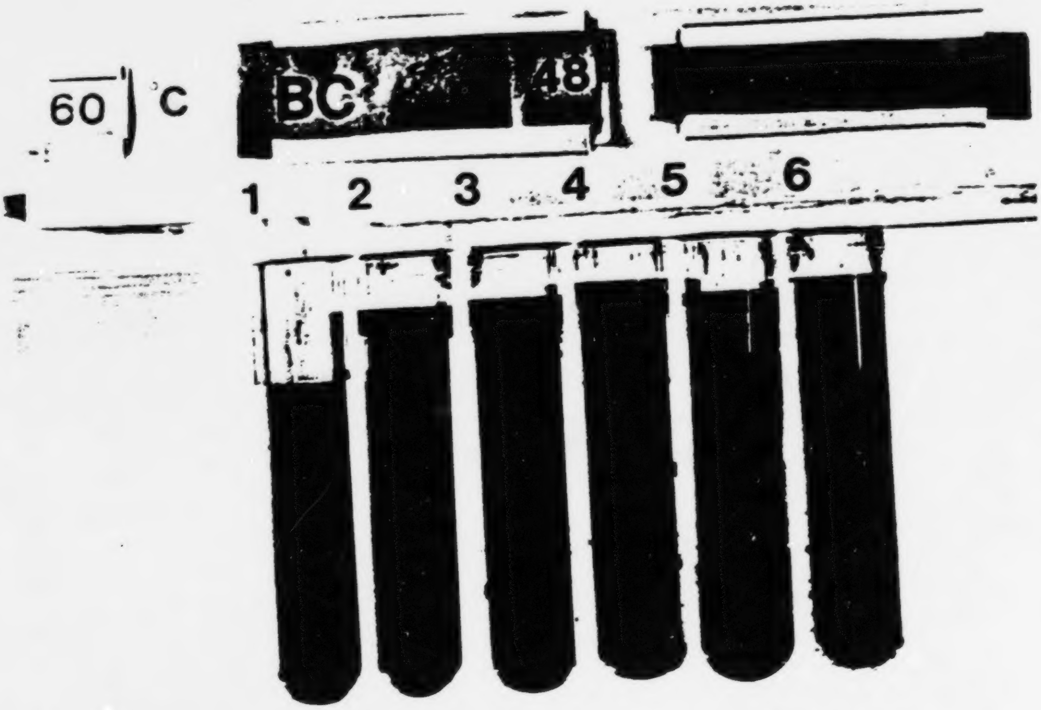
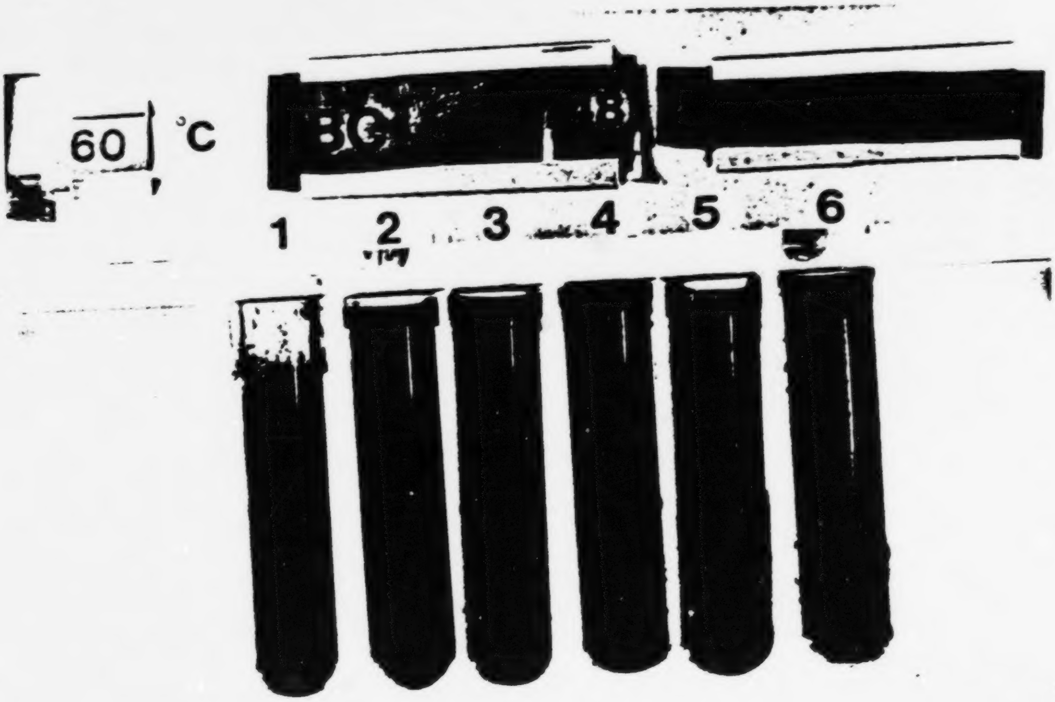

60 °C
BC 48
1
2
3
4
5
6
60 °C
BC 48
1
2
3
4
5
6

Figure 5: Initial screening BC-48


60 °C
BC
48
1
2
3
4
5
6


60 °C
BC
48
1
2
3
4
5
6

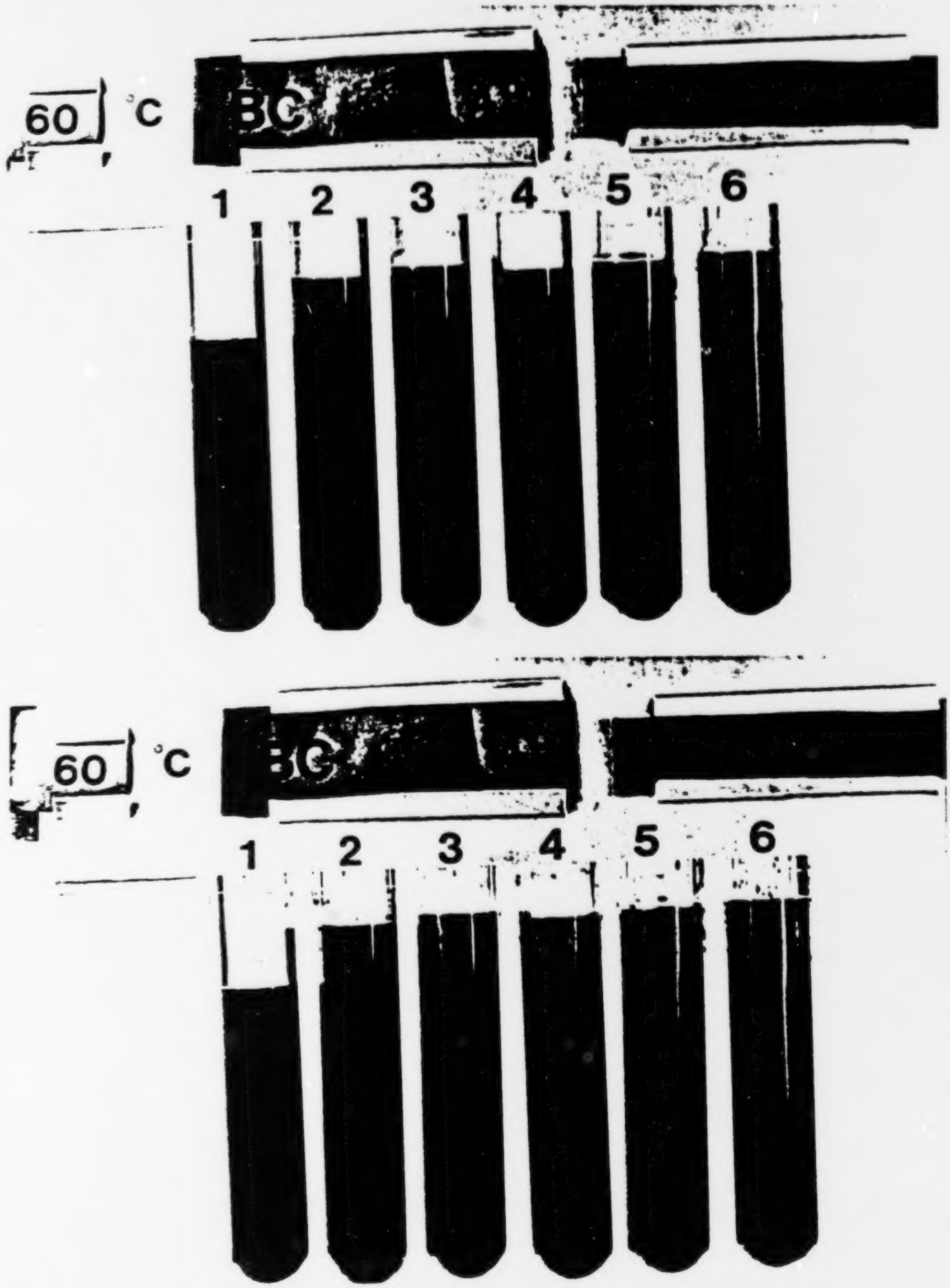
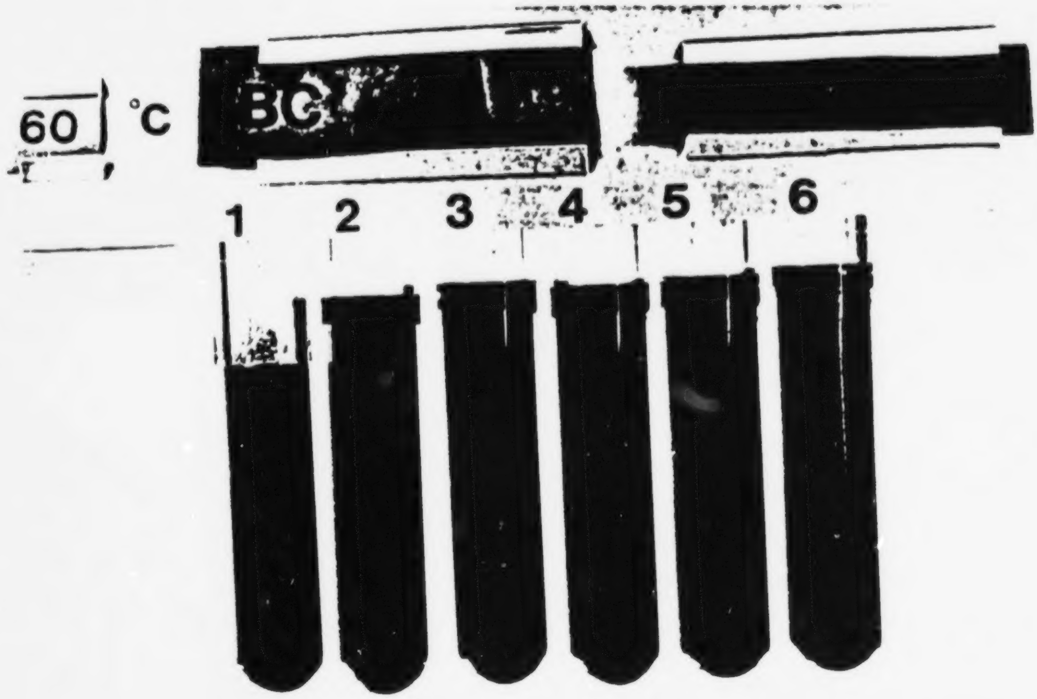
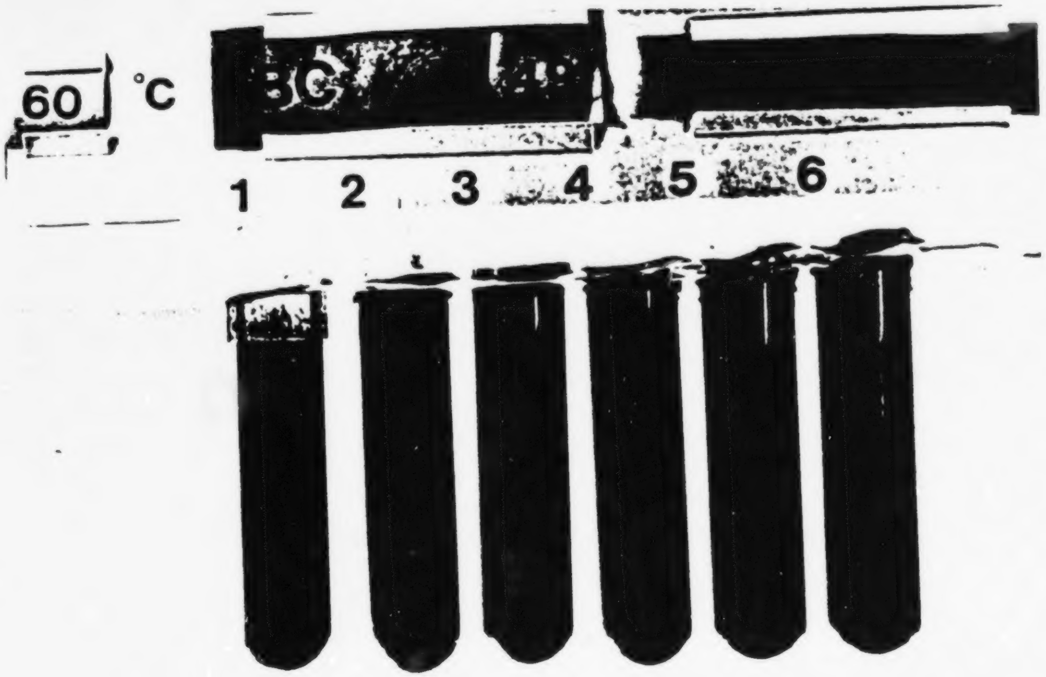

60 °C
BC
1
2
3
4
5
6
60 °C
BC
1
2
3
4
5
6

Figure 6: Initial screening BC-49


60
°C
BC
1
2
3
4
5
6


60
°C
BC
1
2
3
4
5
6

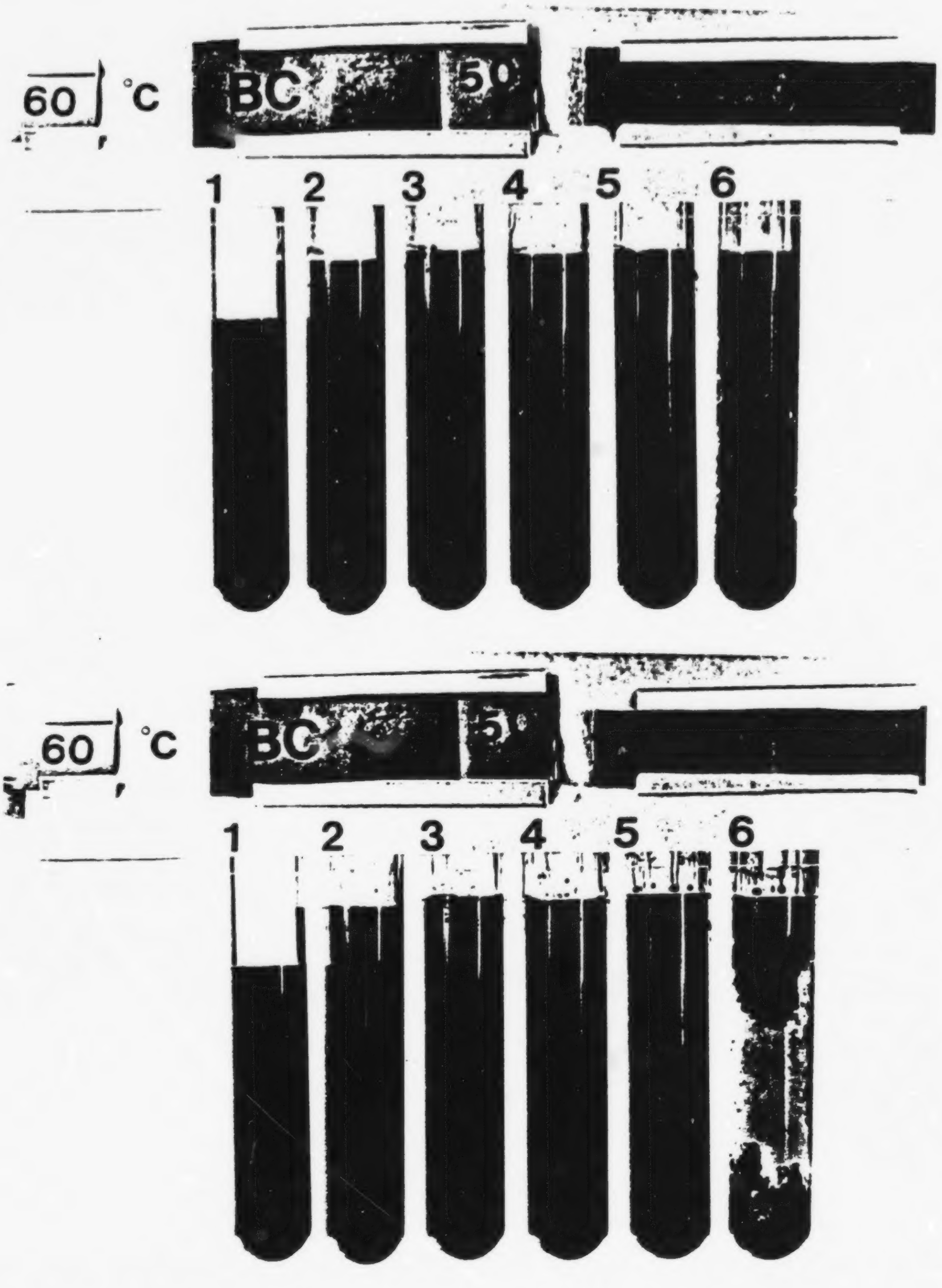
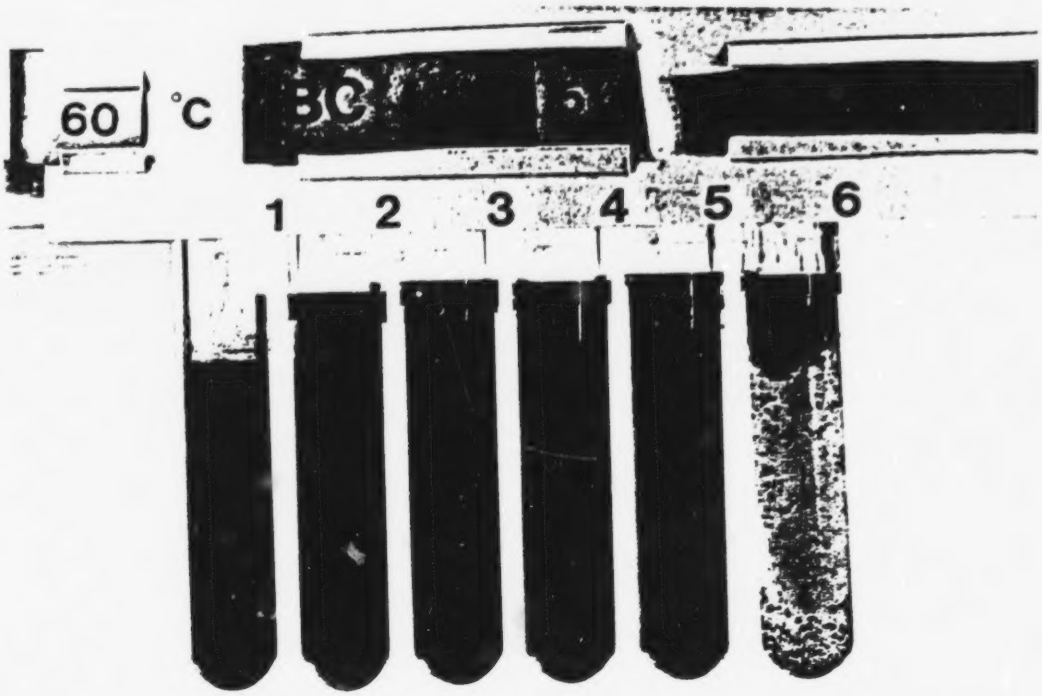
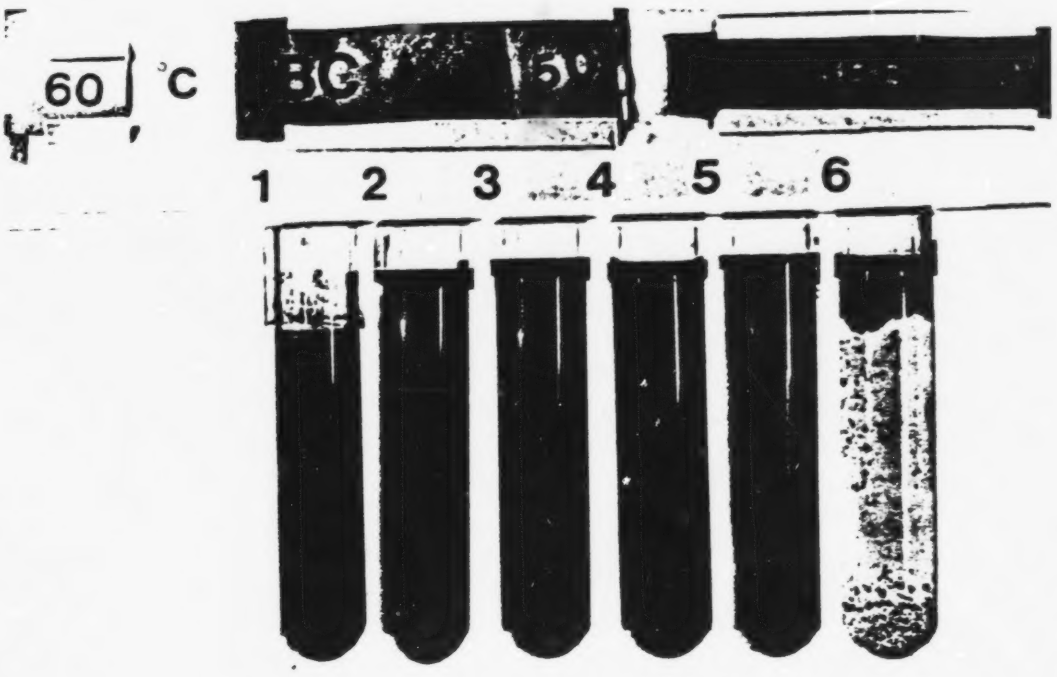

60 °C
BC 50
1
2
3
4
5
6
60 °C
BC 5
1
2
3
4
5
6

Figure [illegible]: Initial sreening BC-50


60 °C
BC
1
2
3
4
5
6


60 °C
BC
1
2
3
4
5
6

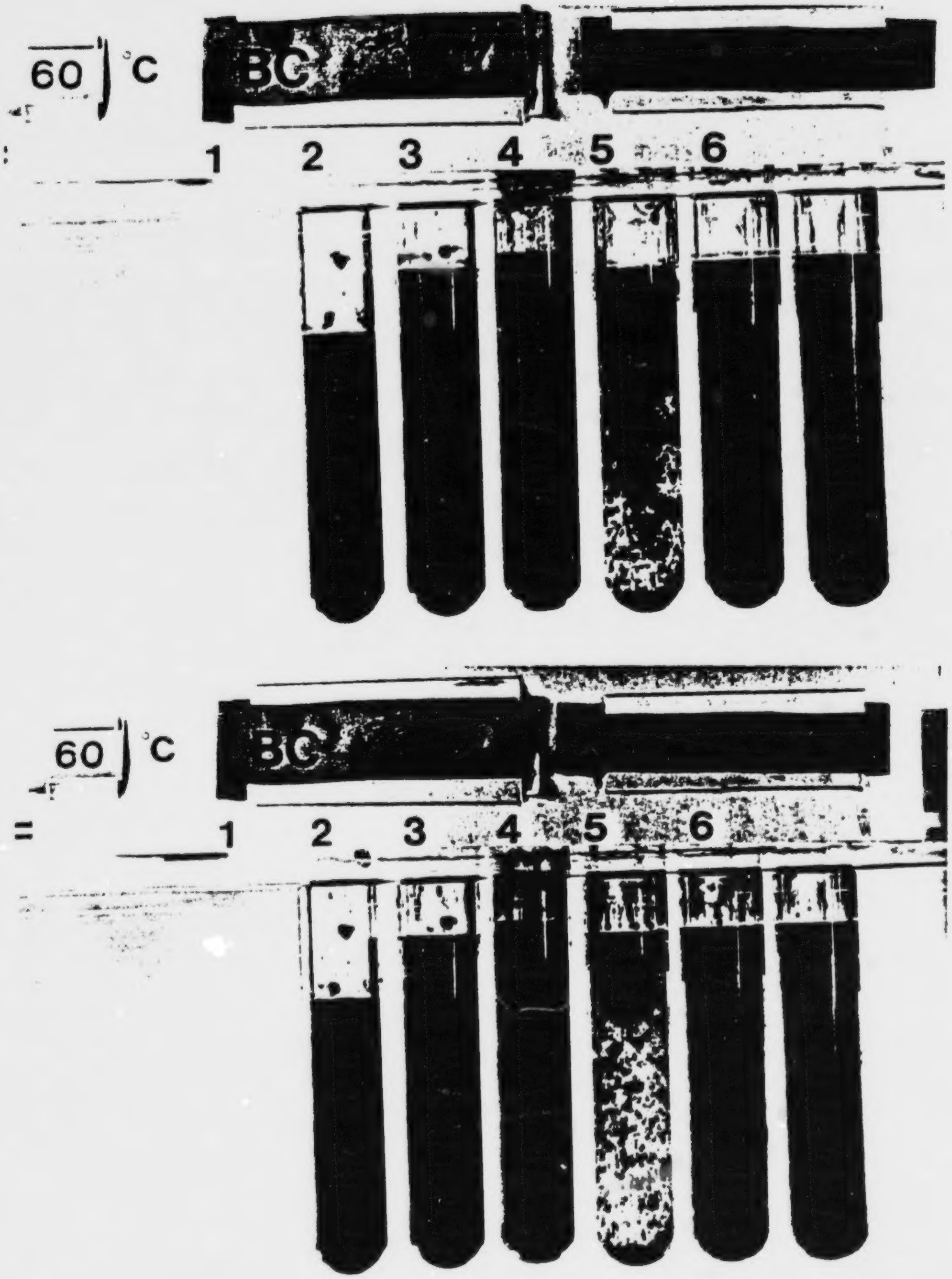
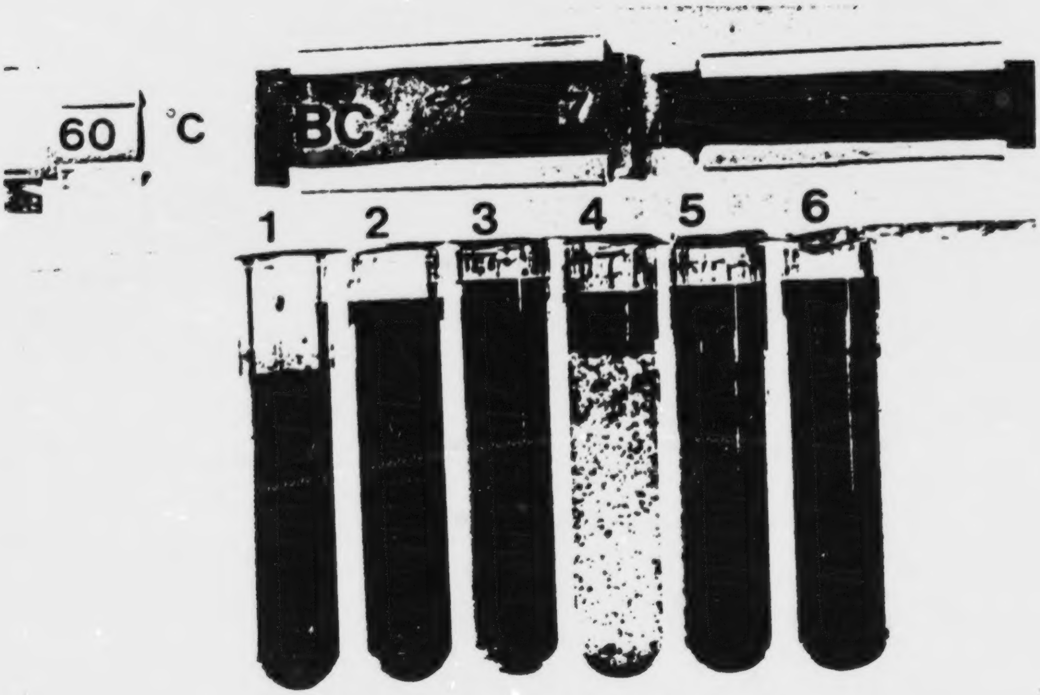
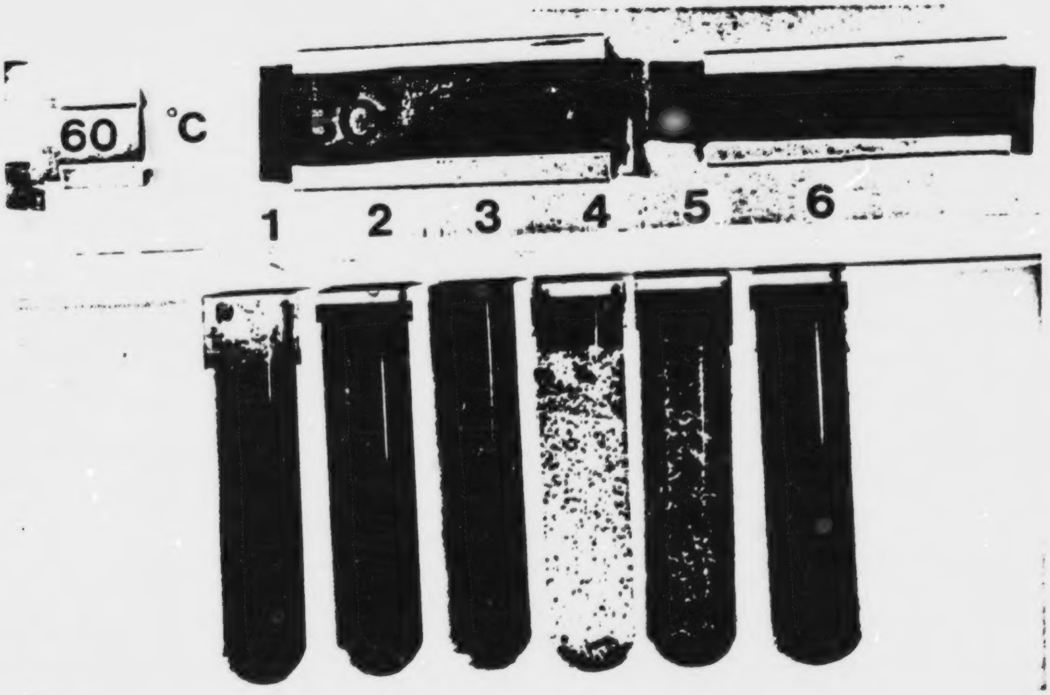

60 °C
BC
1
2
3
4
5
6
60 °C
BC
1
2
3
4
5
6

Figure 8: Initial screening BC-17


60
°C
BC
1
2
3
4
5
6


60
°C
BC
1
2
3
4
5
6

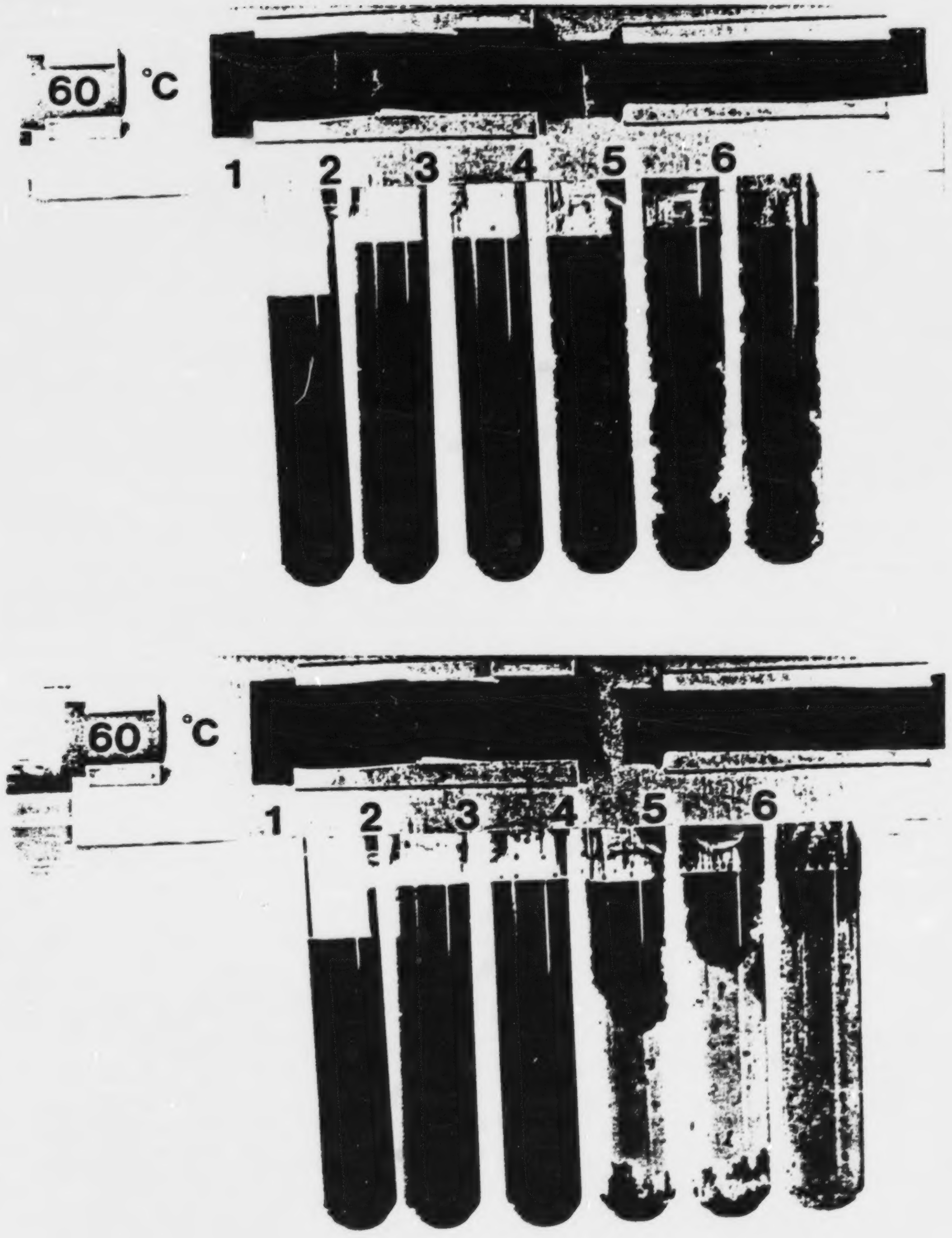
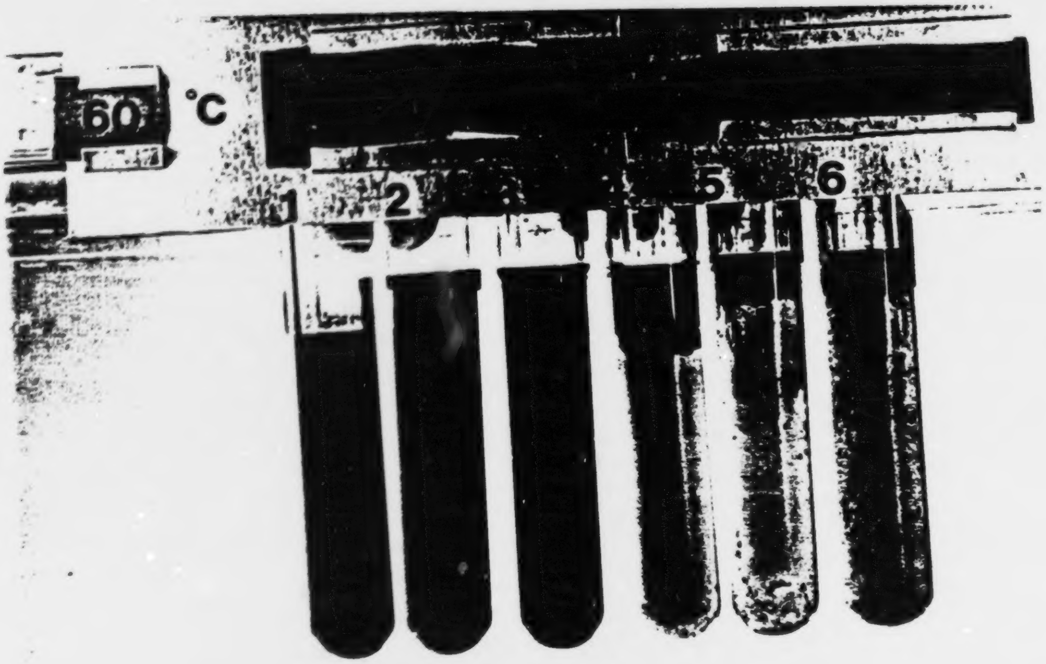
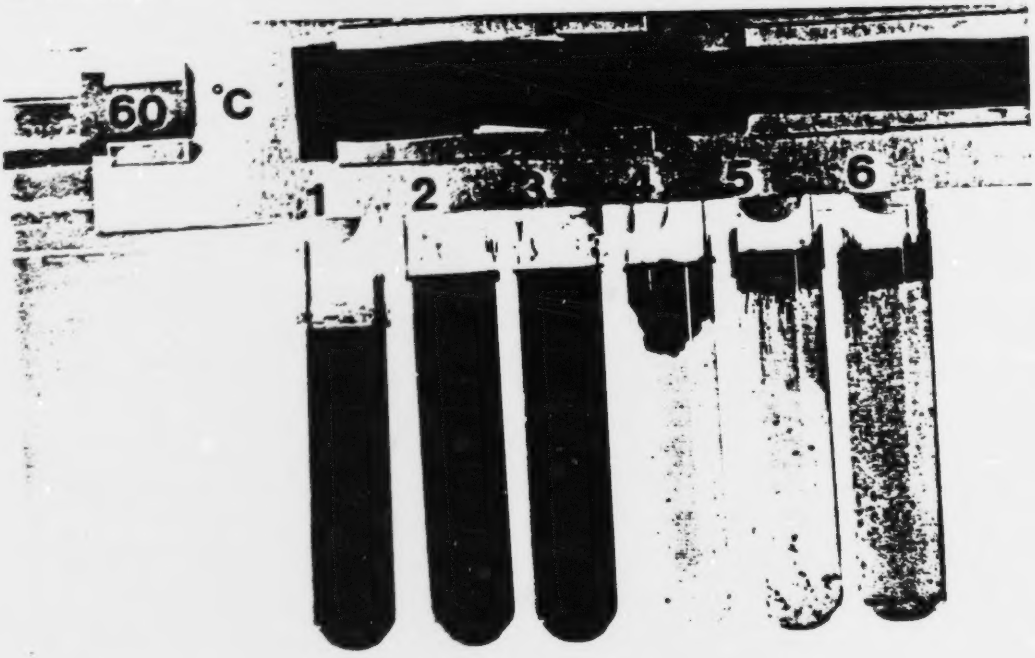

60 °C
1
2
3
4
5
6
60 °C
1
2
3
4
5
6

Figure 9: Solvent optimization, BC-47, 1:1 toluene:bitumen


60 °C
1
2
3
4
5
6


60 °C
1
2
3
4
5
6

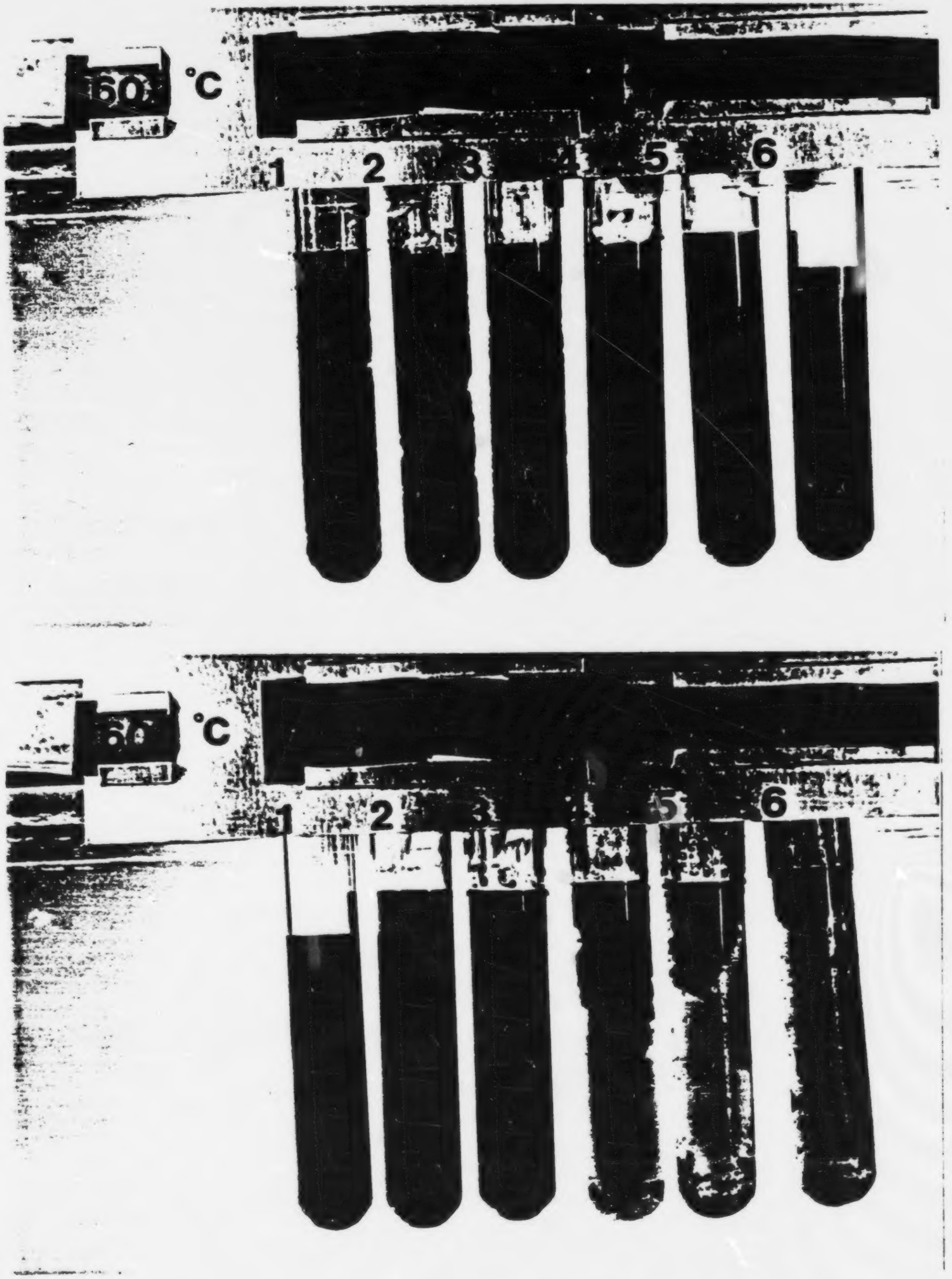
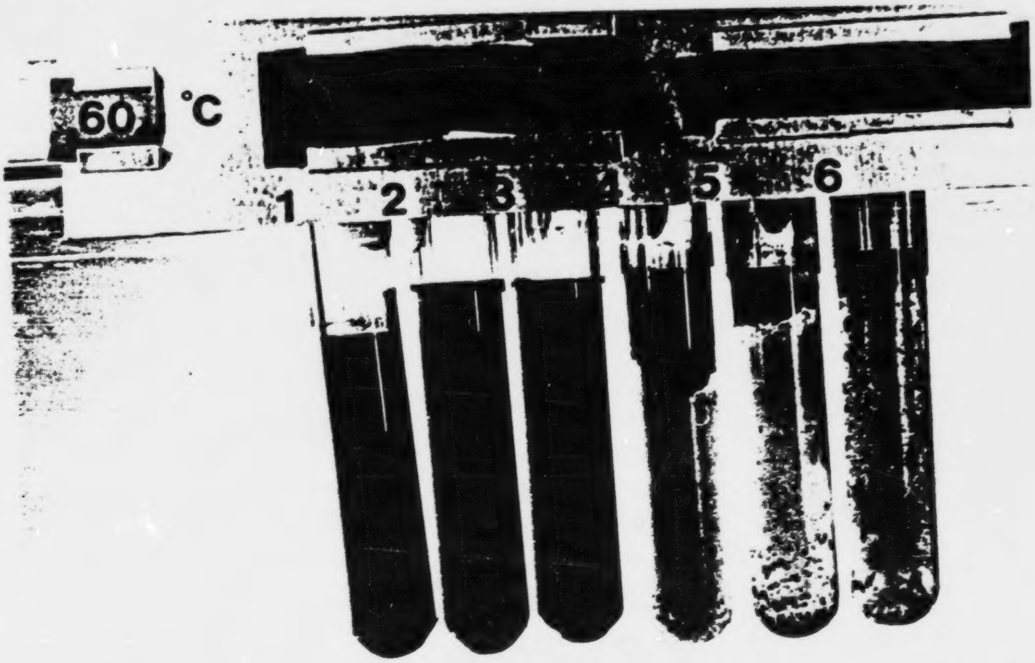
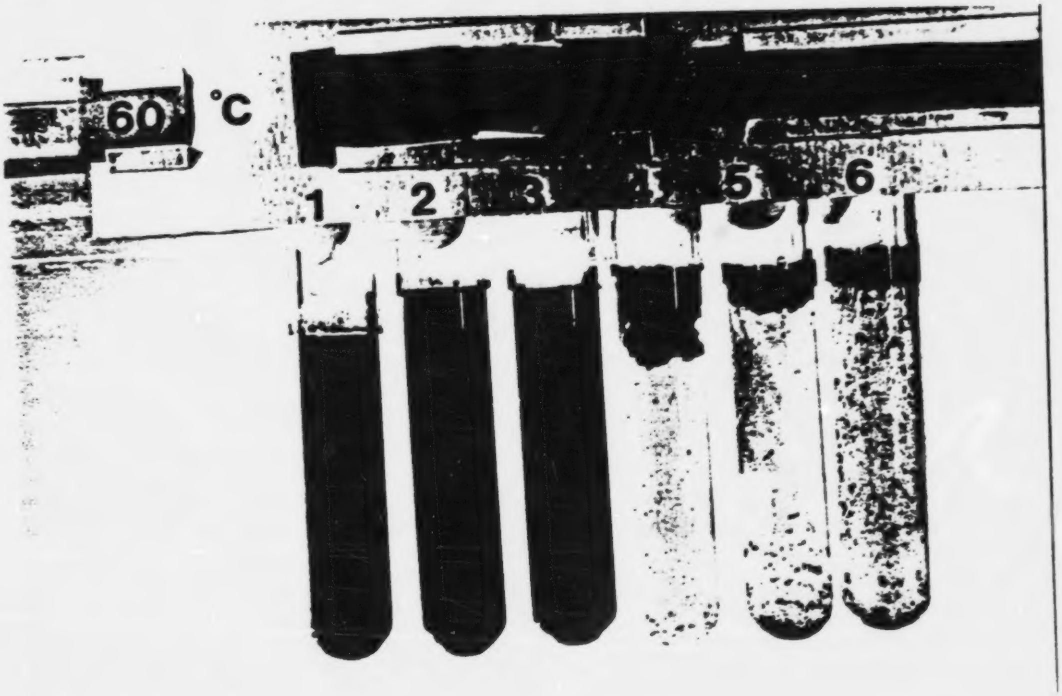

60 °C
1
2
3
4
5
6
60 °C
1
2
3
5
6

Figure 10: Solvent optimization, BC-47, 1:2 toluene:bitumen


60
°C
1
2
3
4
5
6


60
°C
1
2
3
4
5
6

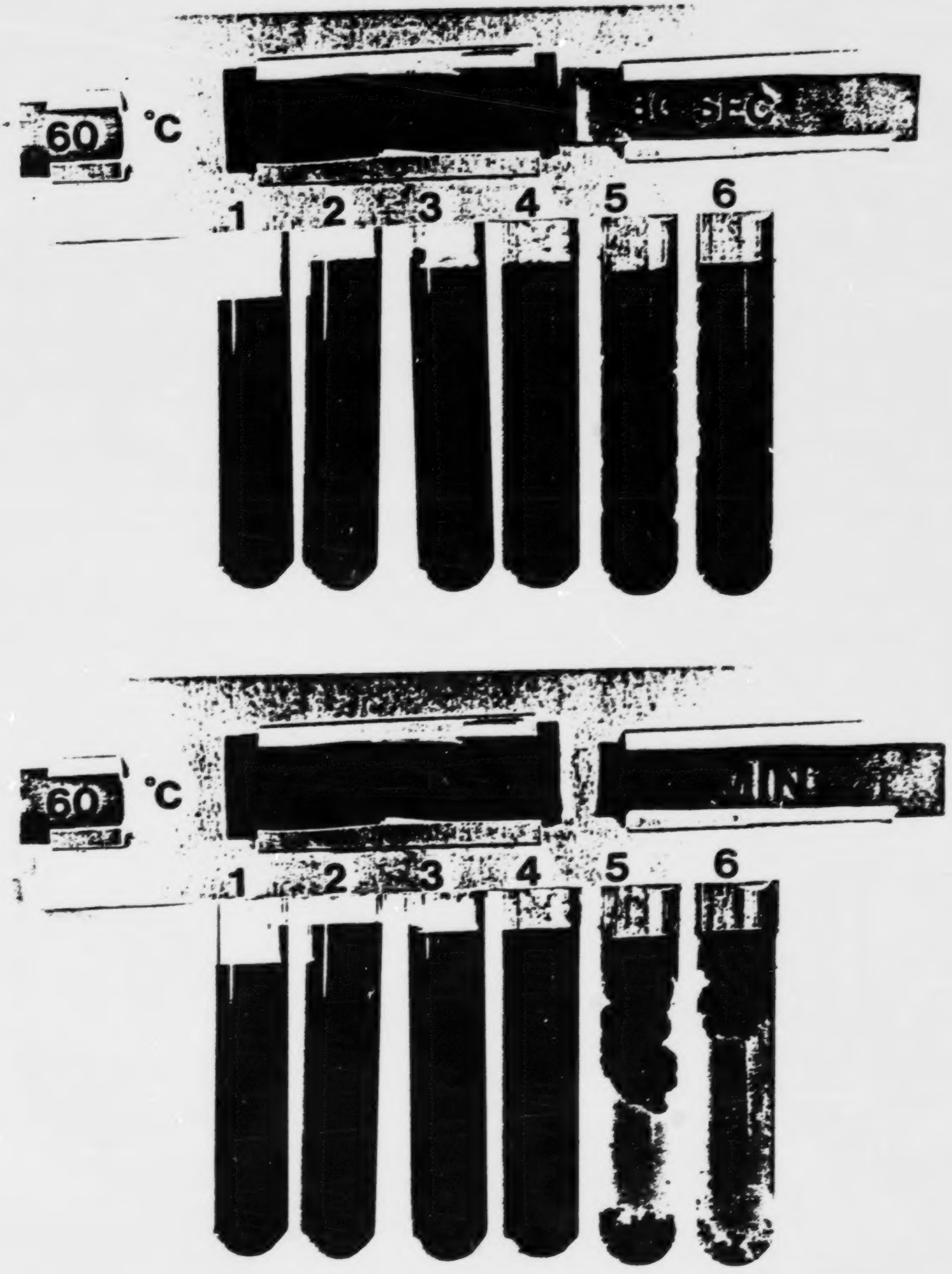
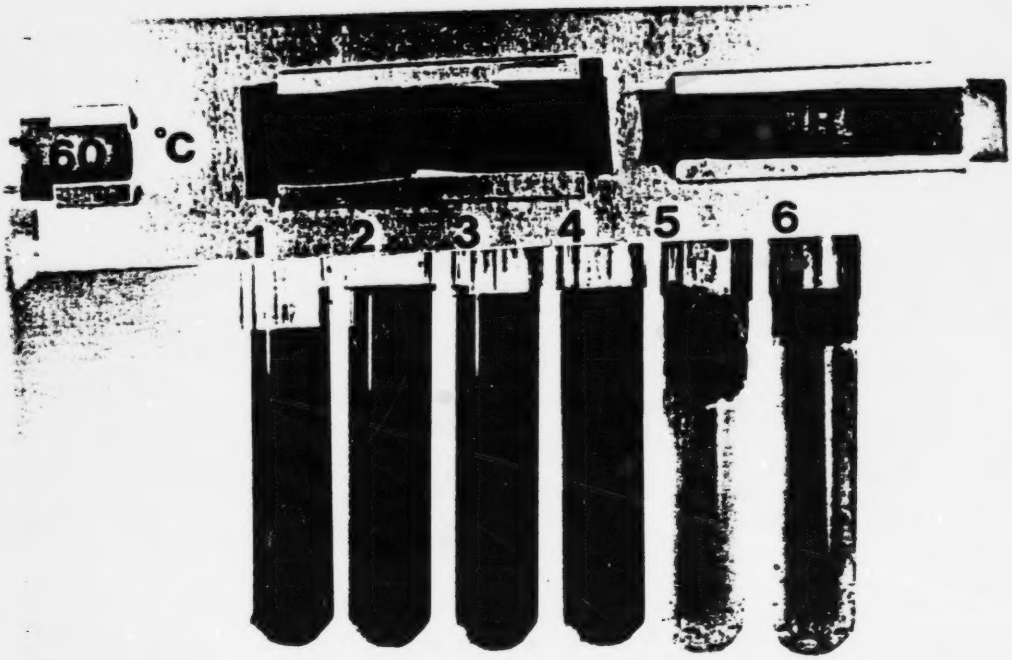
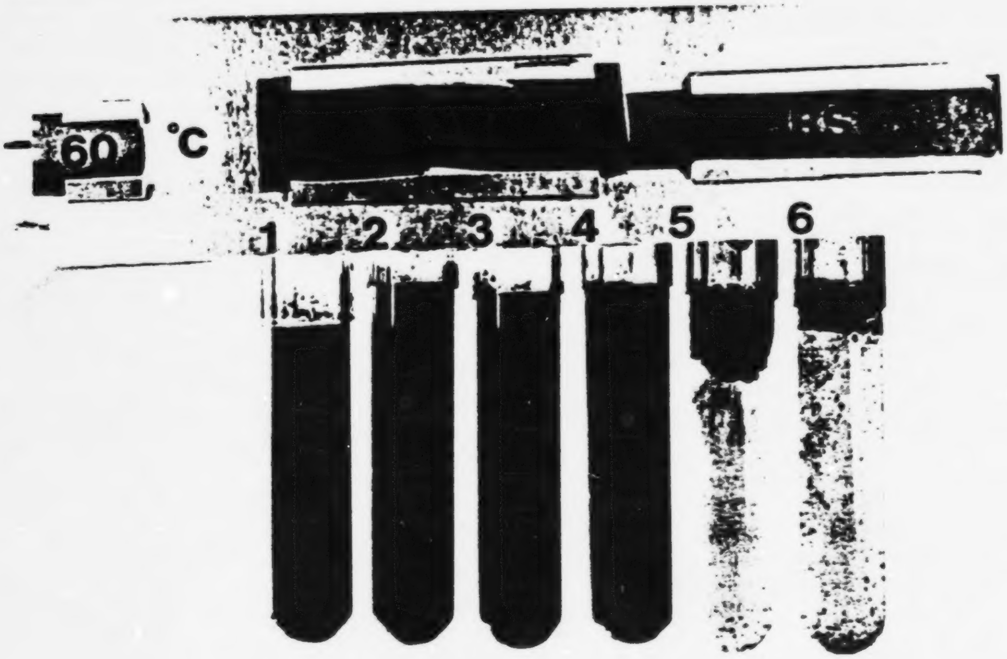

60
°C
SEC
1
2
3
4
5
6
60
°C
MIN
1
2
3
4
5
6

Figure 11: Solvent optimization, BC-47, 1:3 toluene:bitumen


60
°C
1
2
3
4
5
6


60
°C
1
2
3
4
5
6

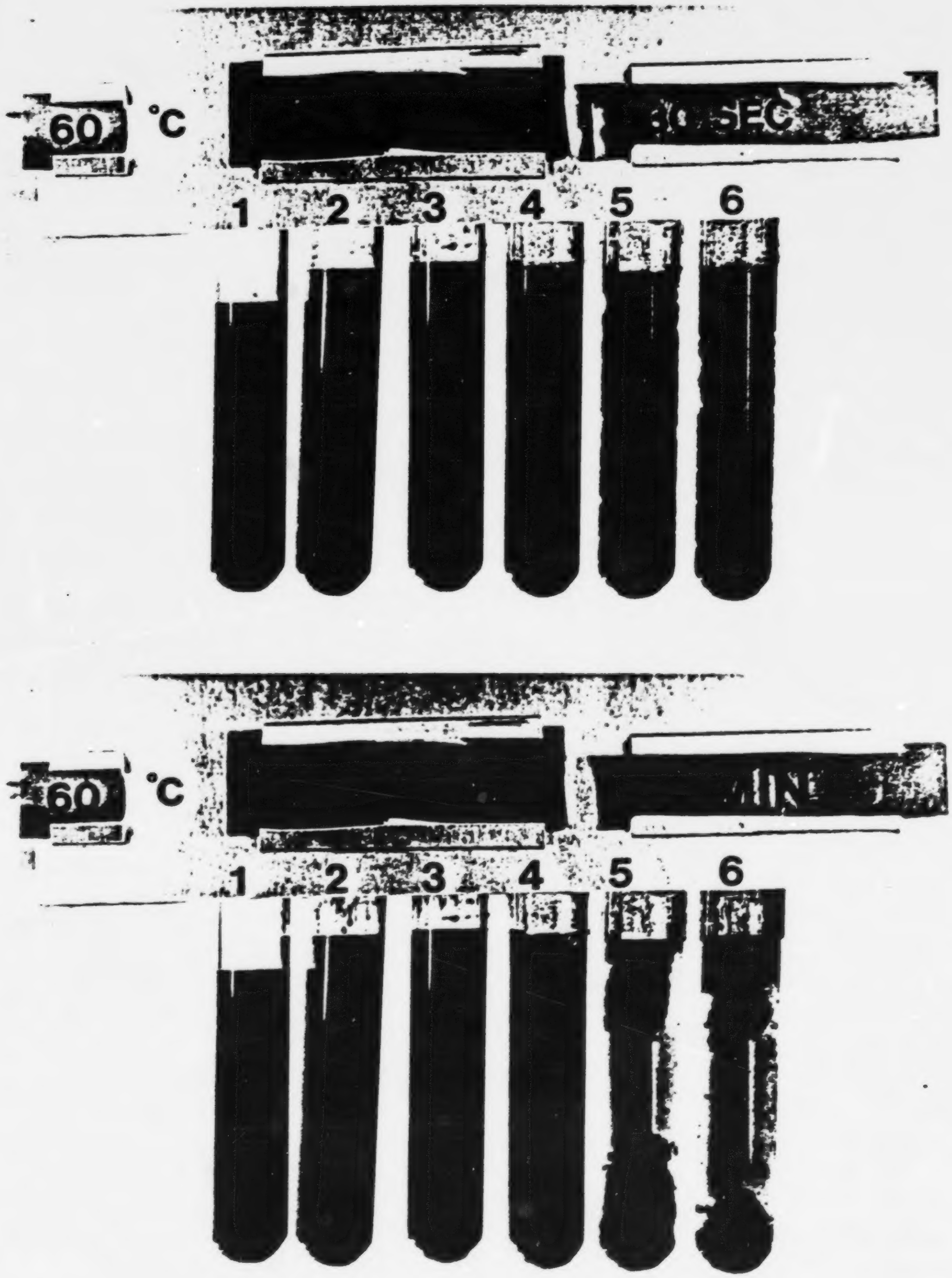
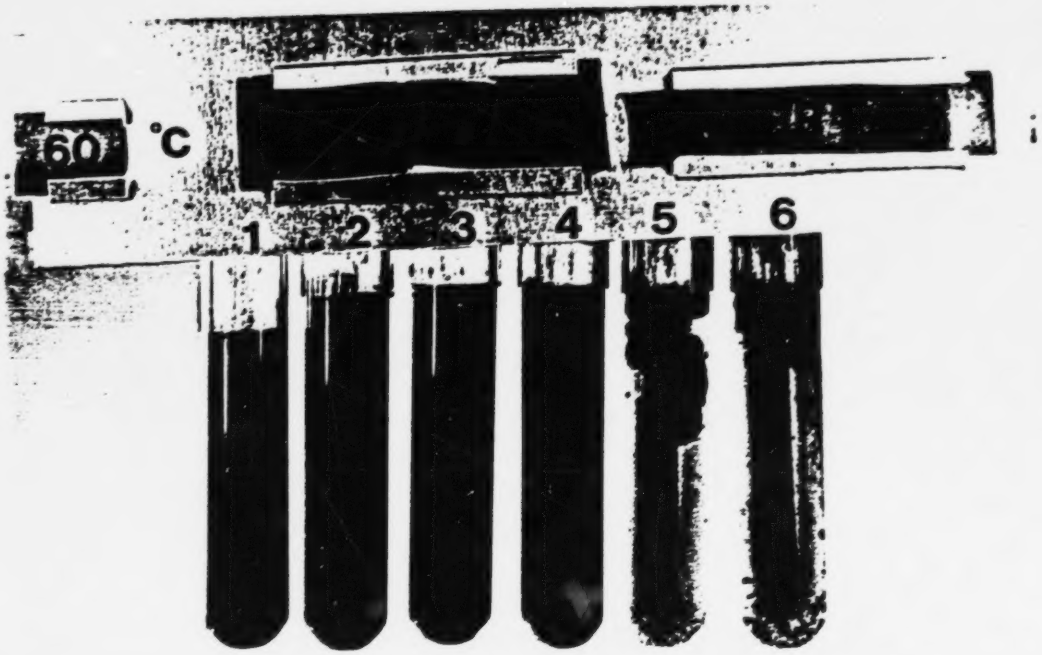
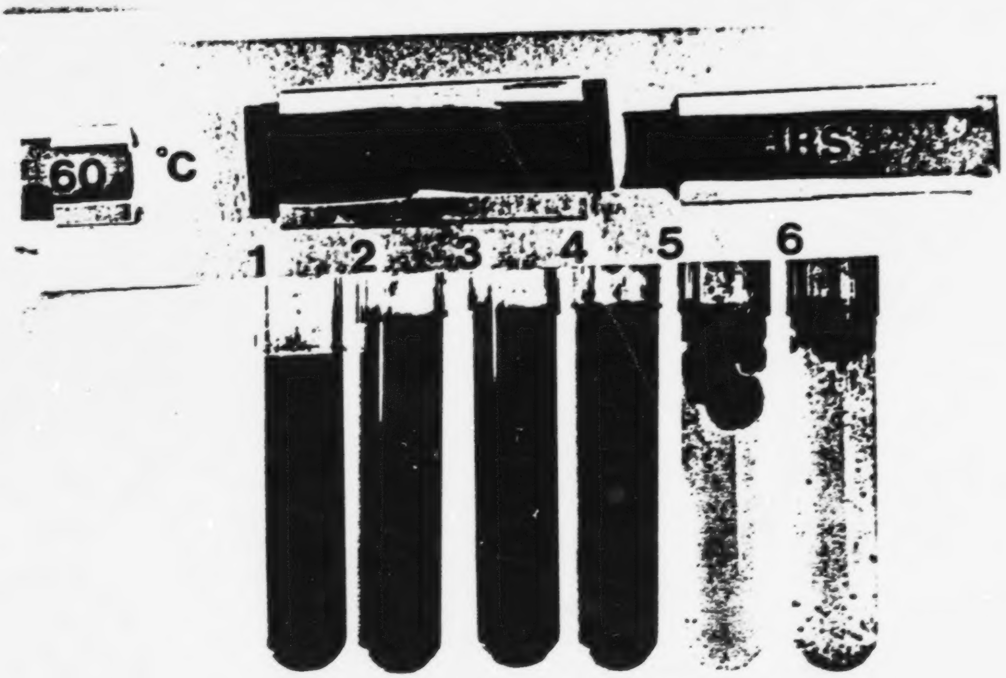

60 °C
SEC
1
2
3
4
5
6
60 °C
MIN
1
2
3
4
5
6

Figure 12: Solvent optimization, BC-47, 1:5 toluene:bitumen


60
°C
1
2
3
4
5
6


60
°C
BS
1
2
3
4
5
6

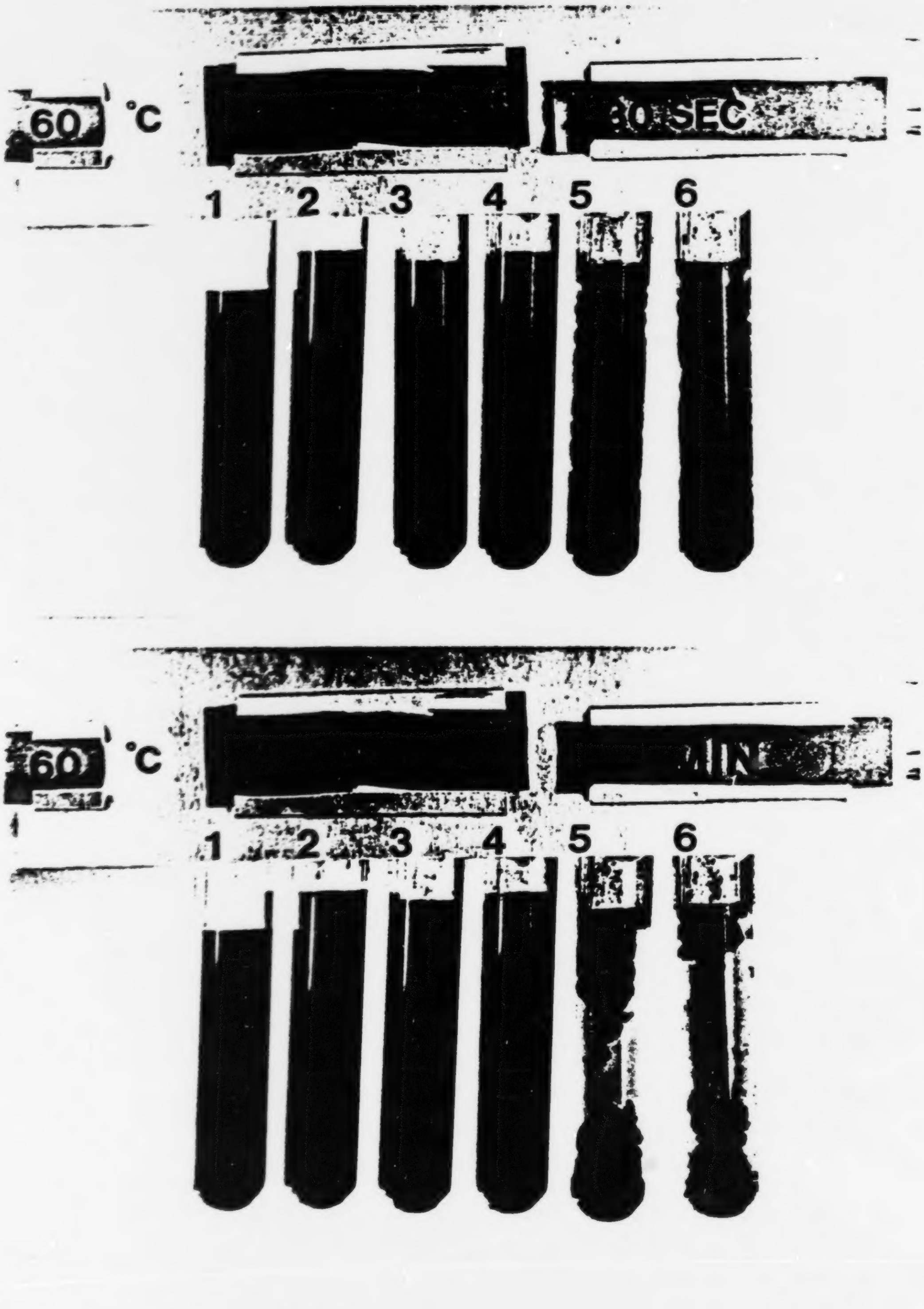
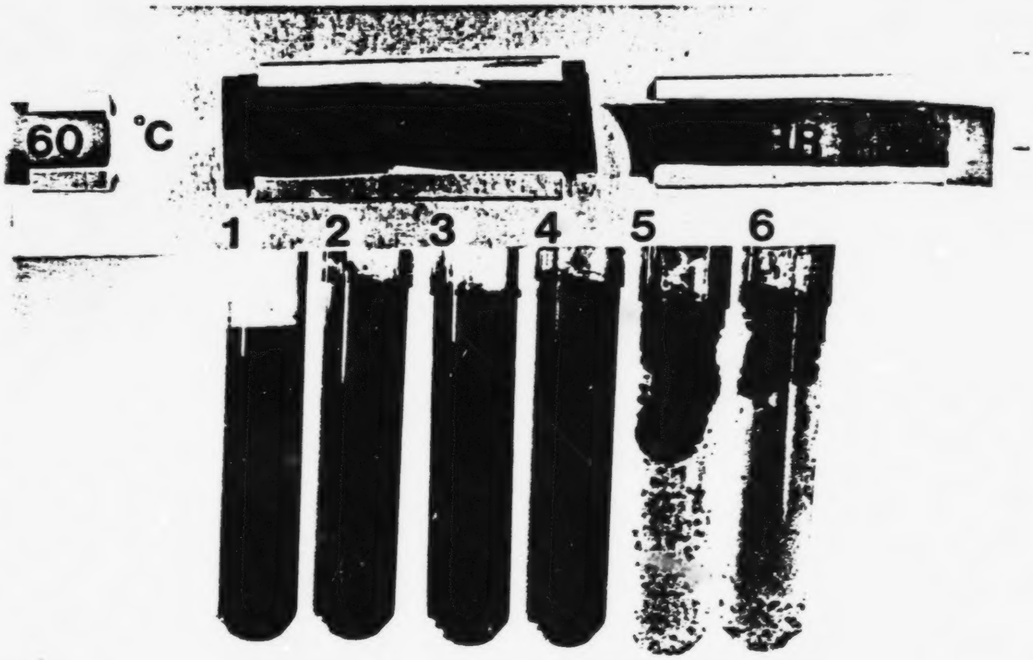
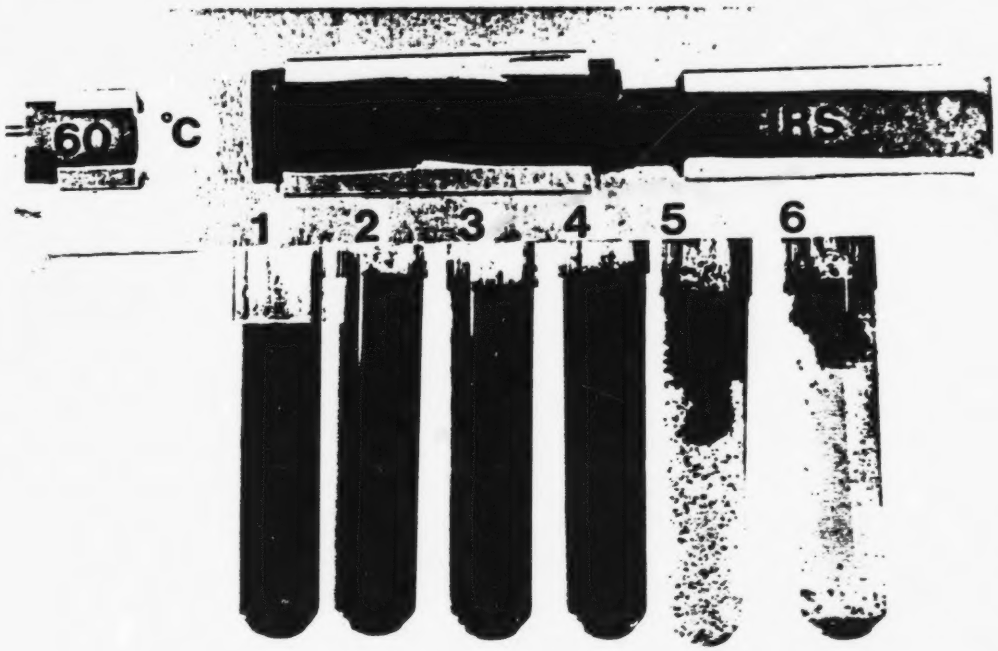

60 °C
30 SEC
1
2
3
4
5
6
60 °C
MIN
1
2
3
4
5
6

Figure 13: Solvent optimization, BC-47, 1:10 toluene:bitumen


60 °C
1
2
3
4
5
6


60 °C
RS
1
2
3
4
5
6

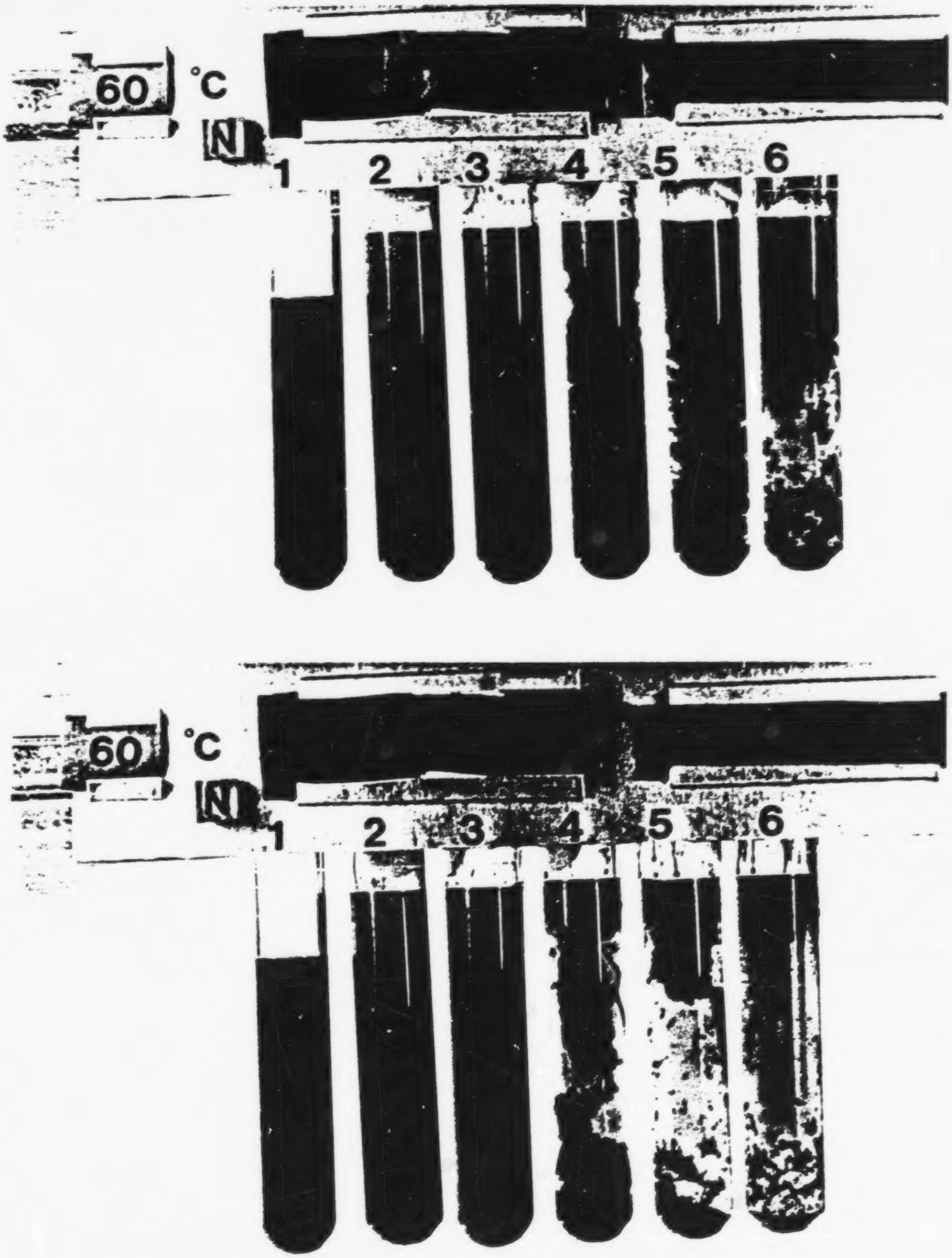
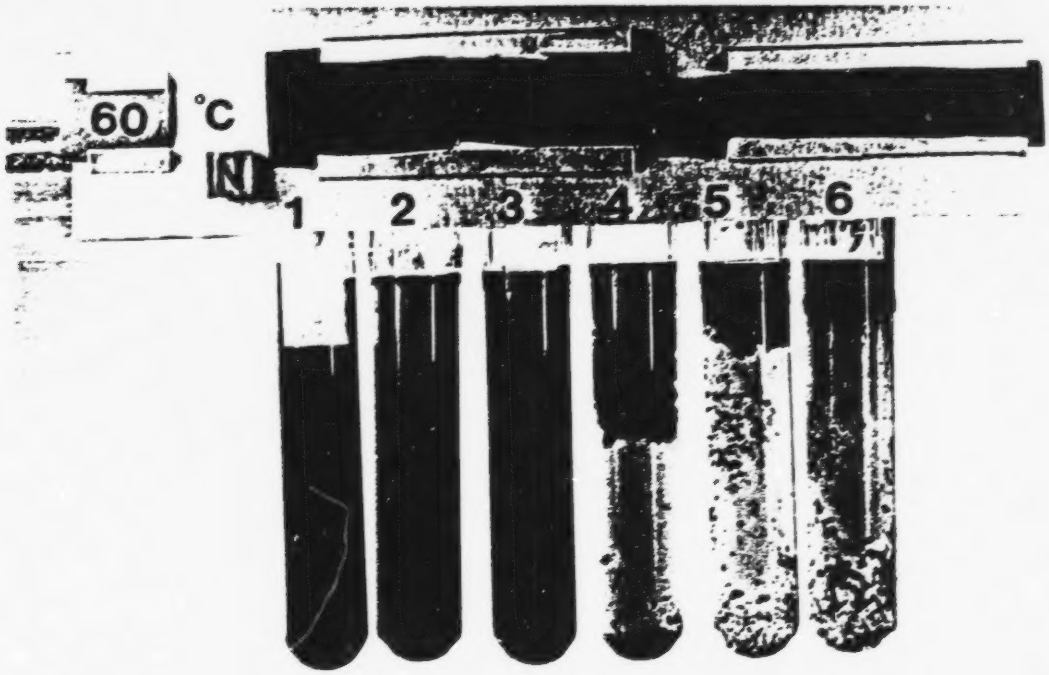
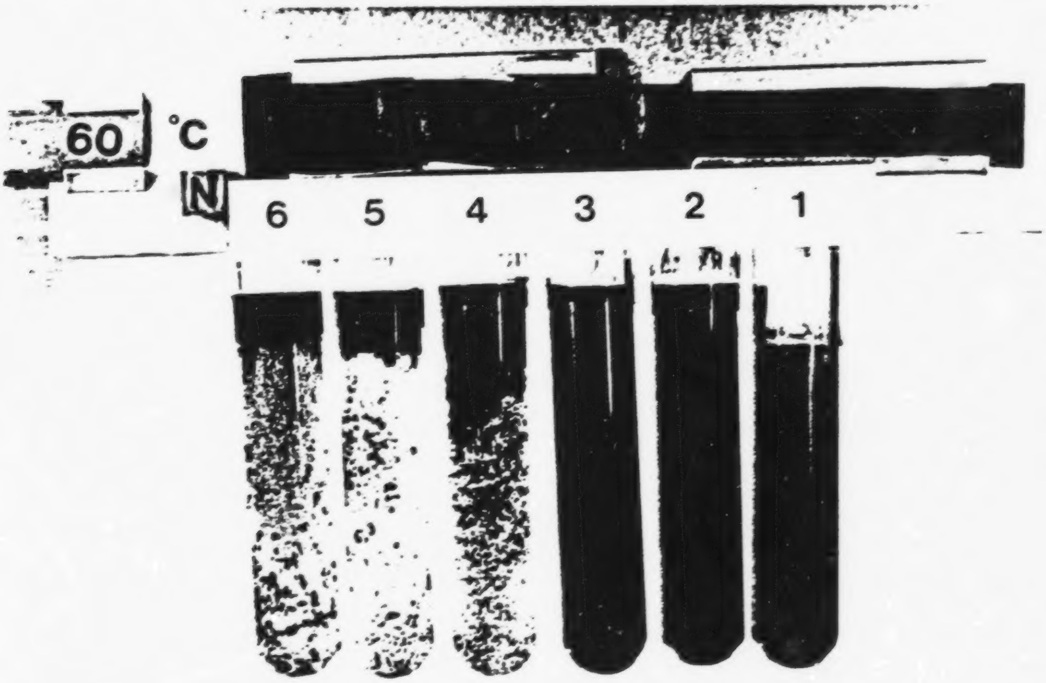

60 °C
N
1
2
3
4
5
6
60 °C
N
1
2
3
4
5
6

Figure 14: Solvent optimization, BC-47, 2:1 naphtha:bitumen


60 °C
N
1
2
3
4
5
6


60 °C
N
6
5
4
3
2
1

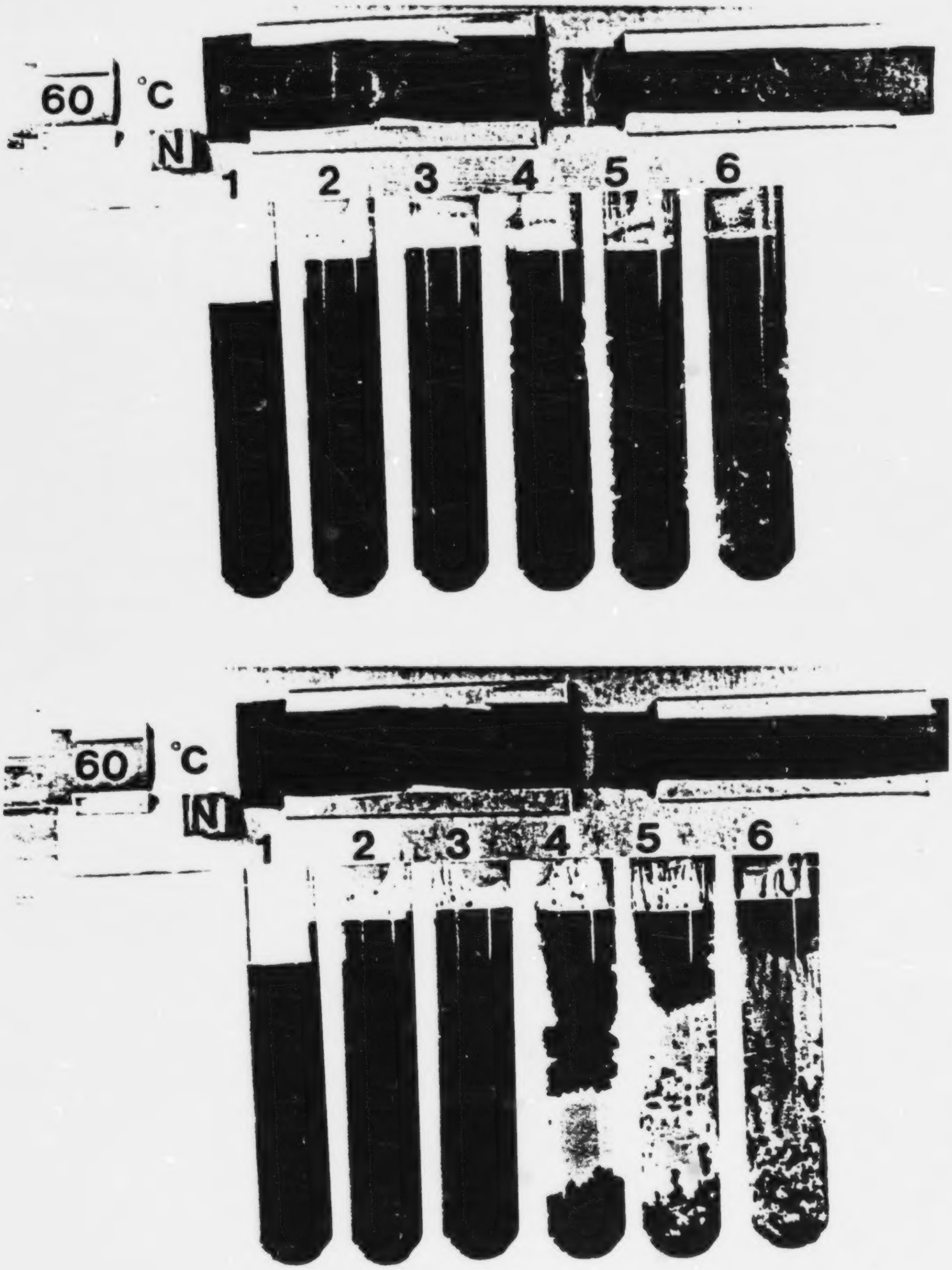
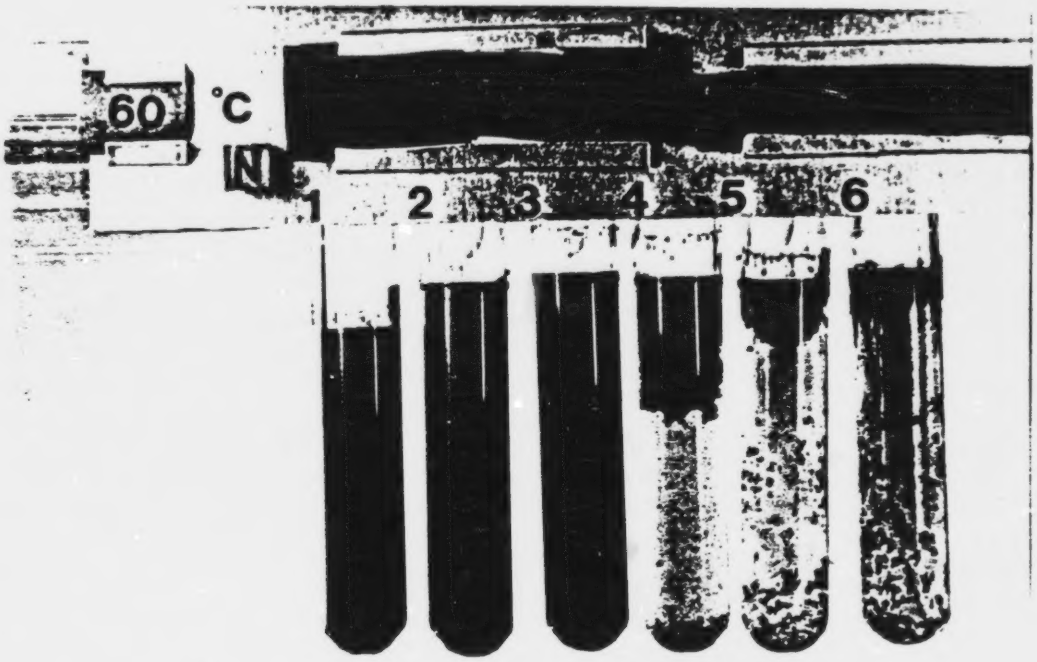
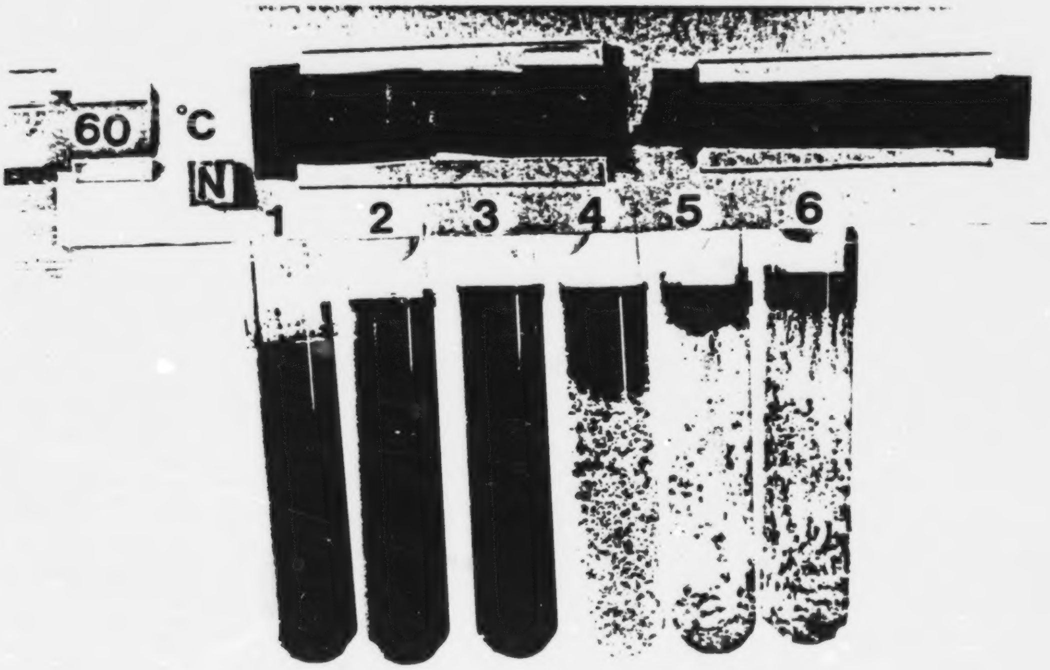

60 °C
N
1
2
3
4
5
6
60 °C
N
1
2
3
4
5
6

Figure 15: Solvent optimization, BC-47, 1:1 naphtha:bitumen


60
°C
N
1
2
3
4
5
6


60
°C
N
1
2
3
4
5
6

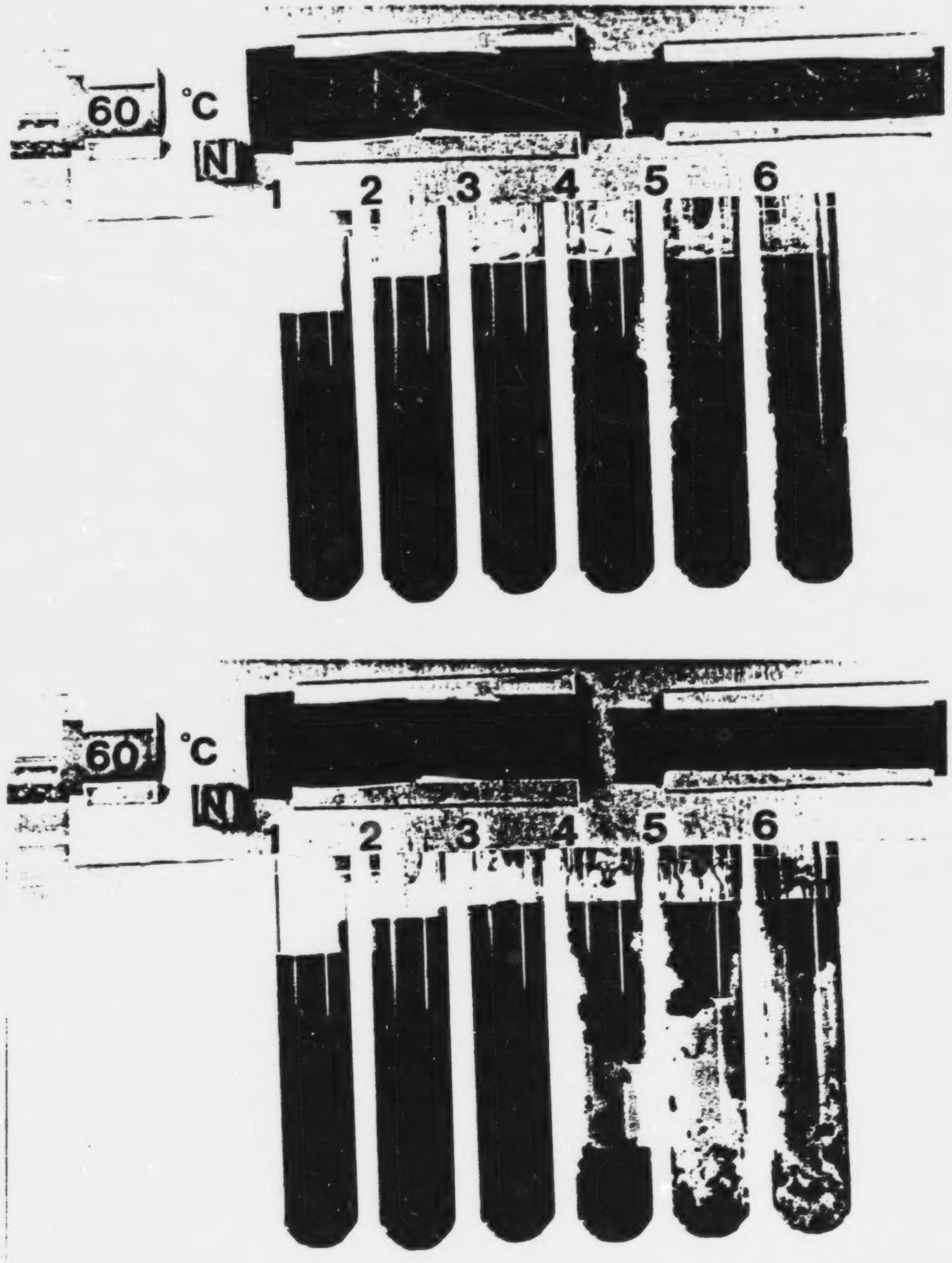
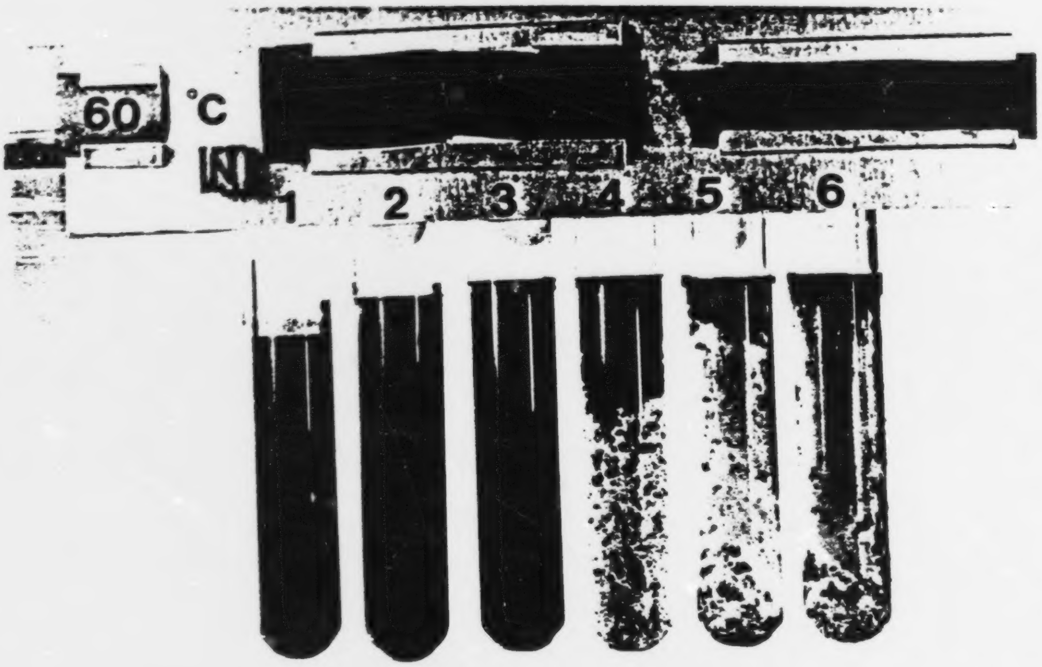
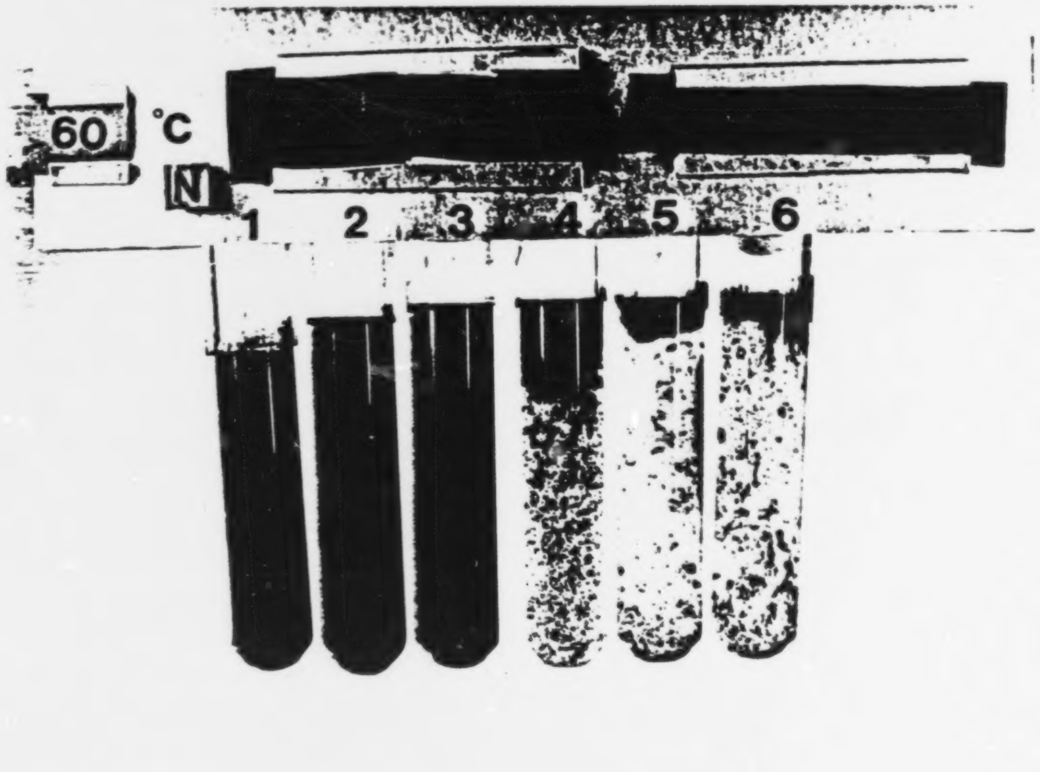

60 °C
N
1
2
3
4
5
6
60 °C
N
1
2
3
4
5
6

Figure 16: Solvent optimization, BC-47, 1:2 naphtha:bitumen


60 °C
N
1
2
3
4
5
6


60 °C
N
1
2
3
4
5
6

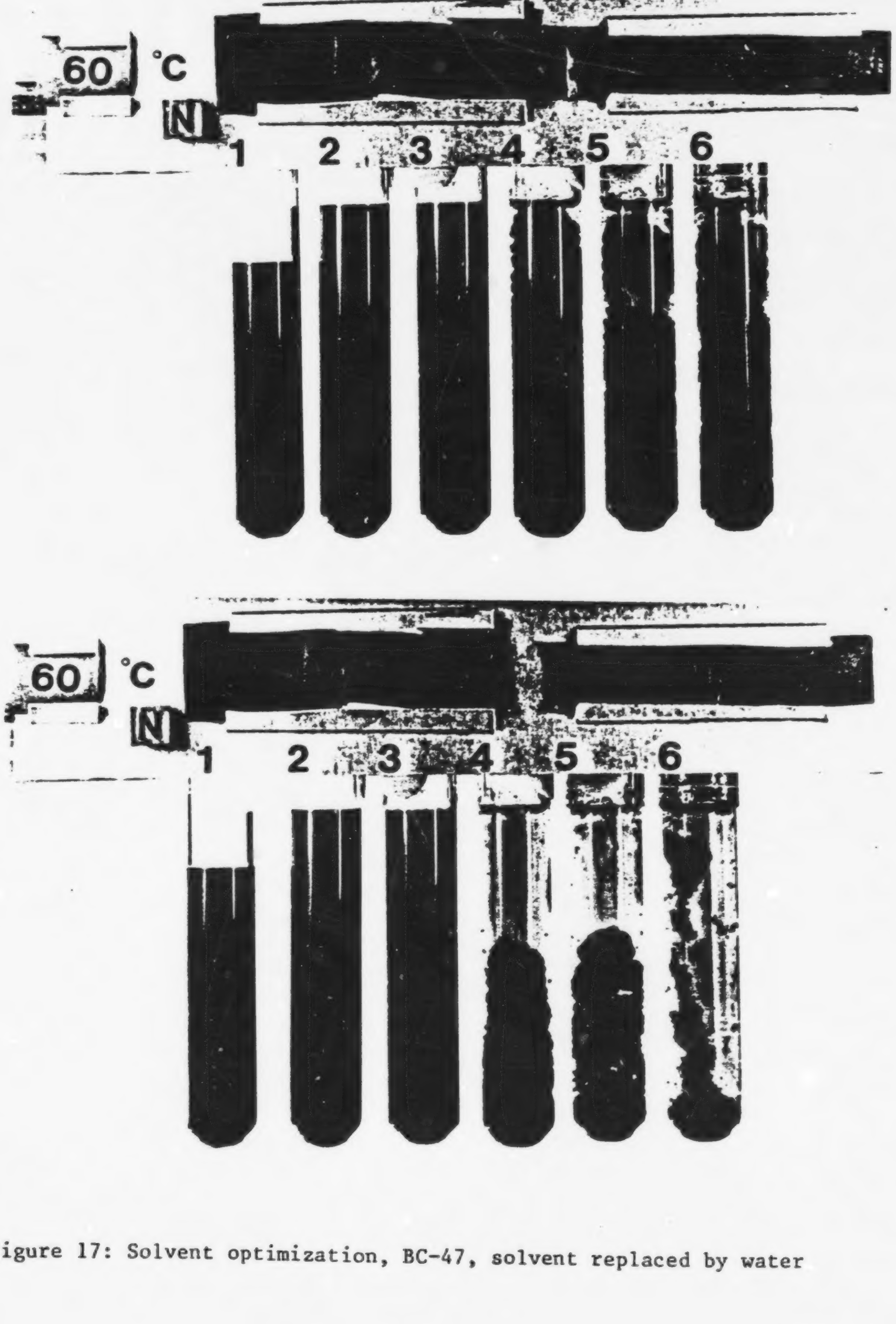
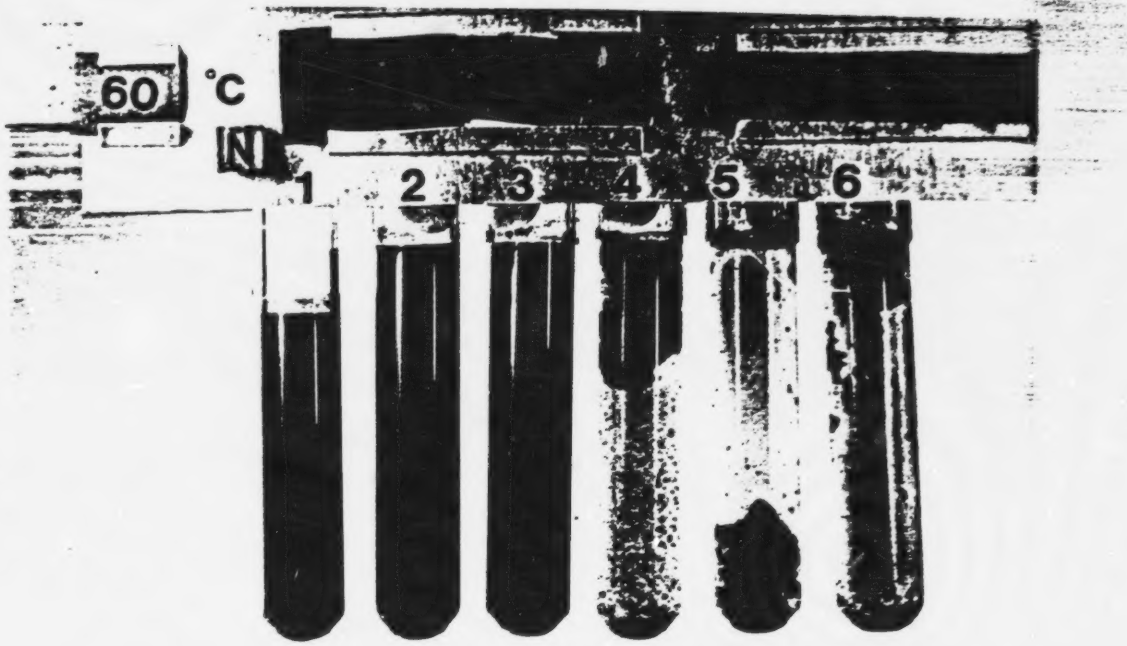
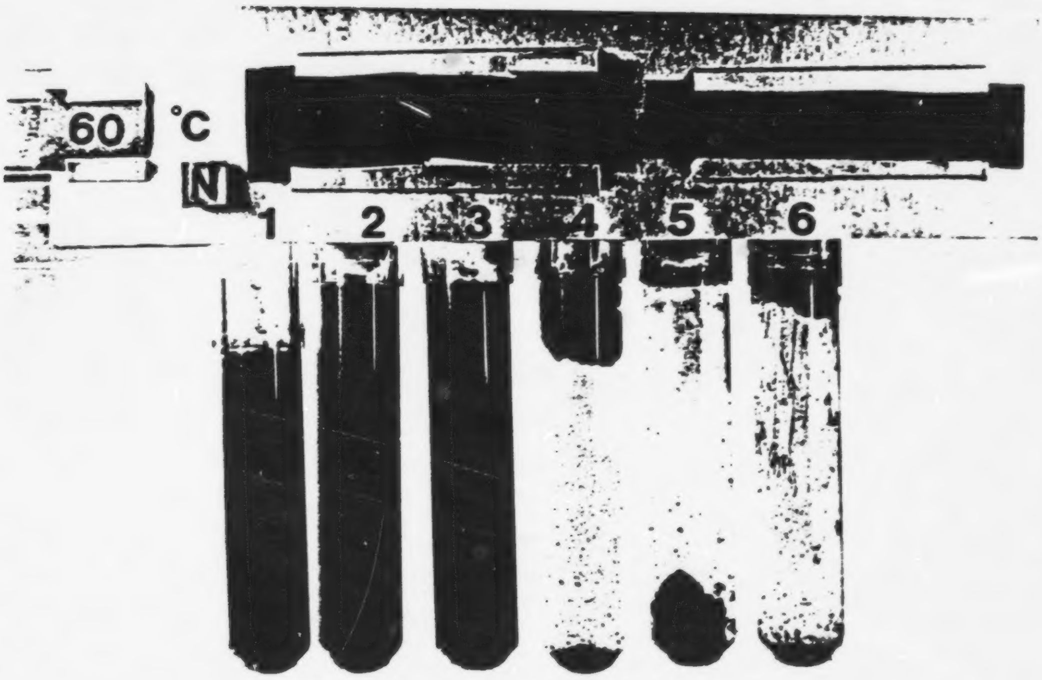

60 °C
N
1
2
3
4
5
6
60 °C
N
1
2
3
4
5
6

Figure 17: Solvent optimization, BC-47, solvent replaced by water


60
°C
N
1
2
3
4
5
6


60
°C
N
1
2
3
4
5
6

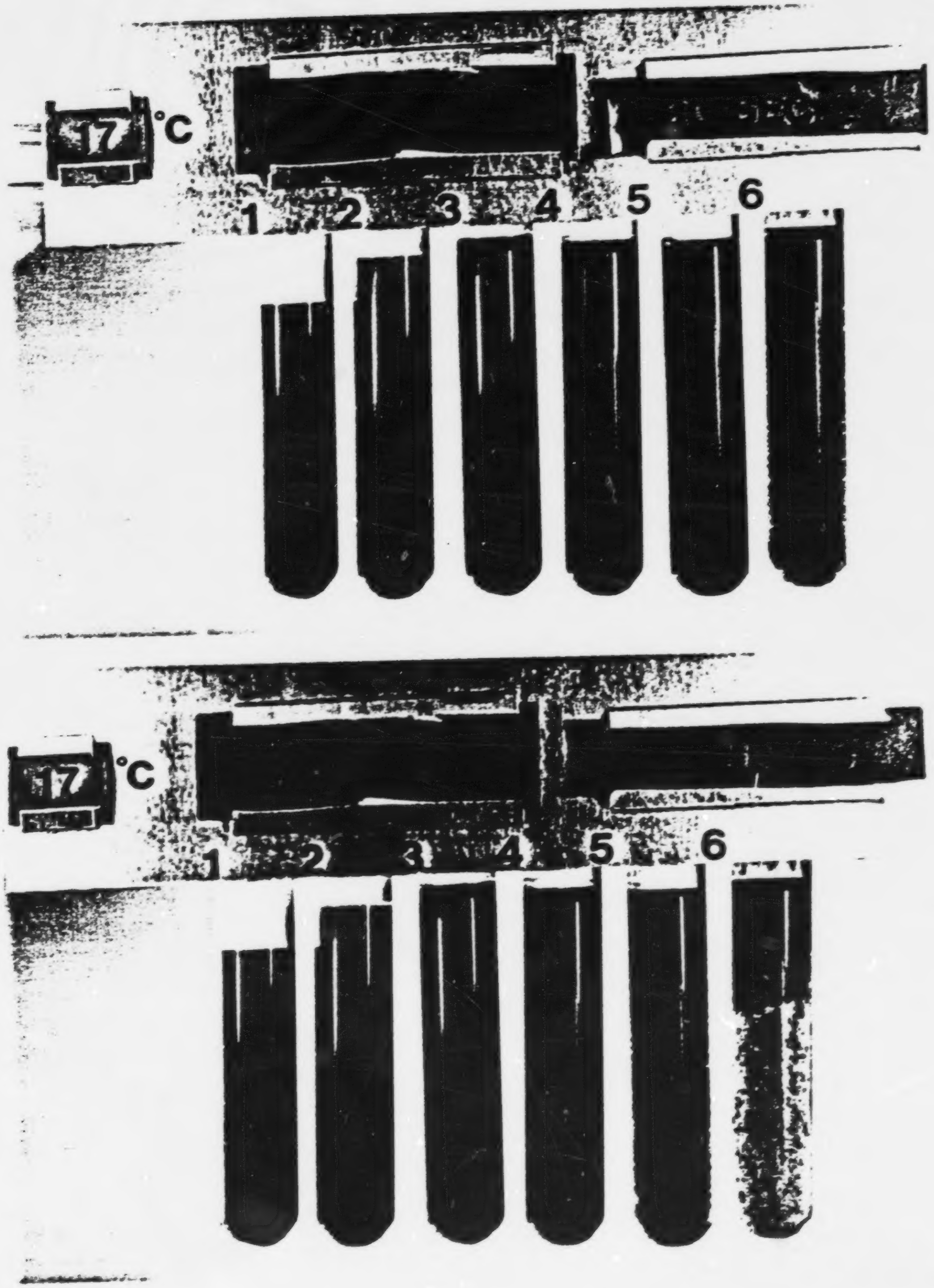
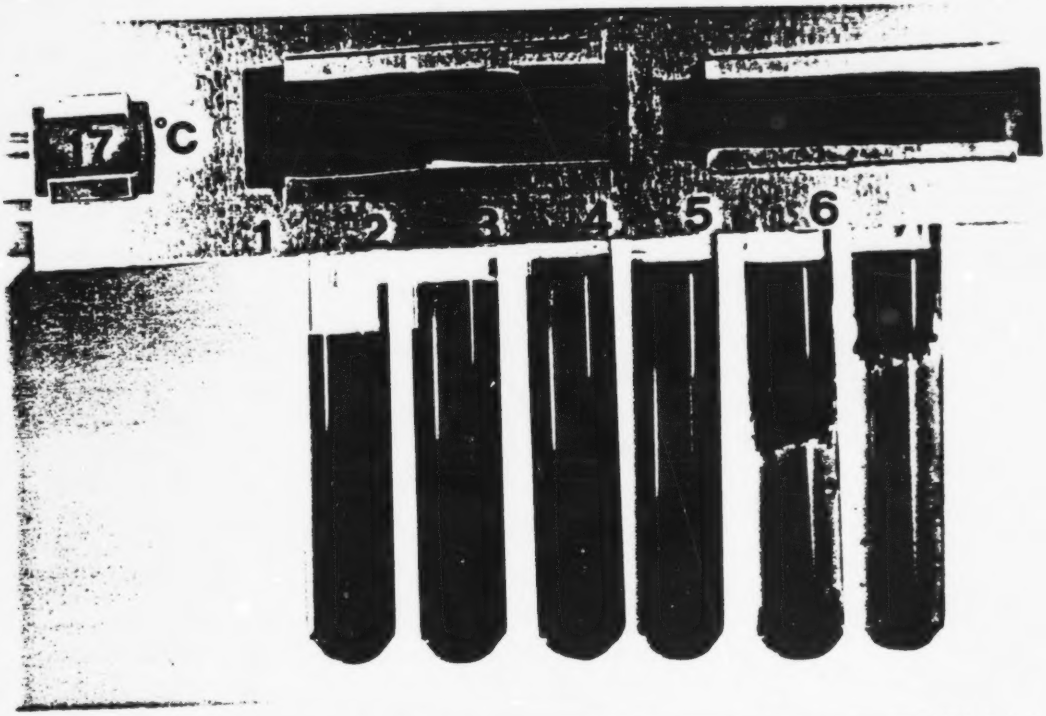
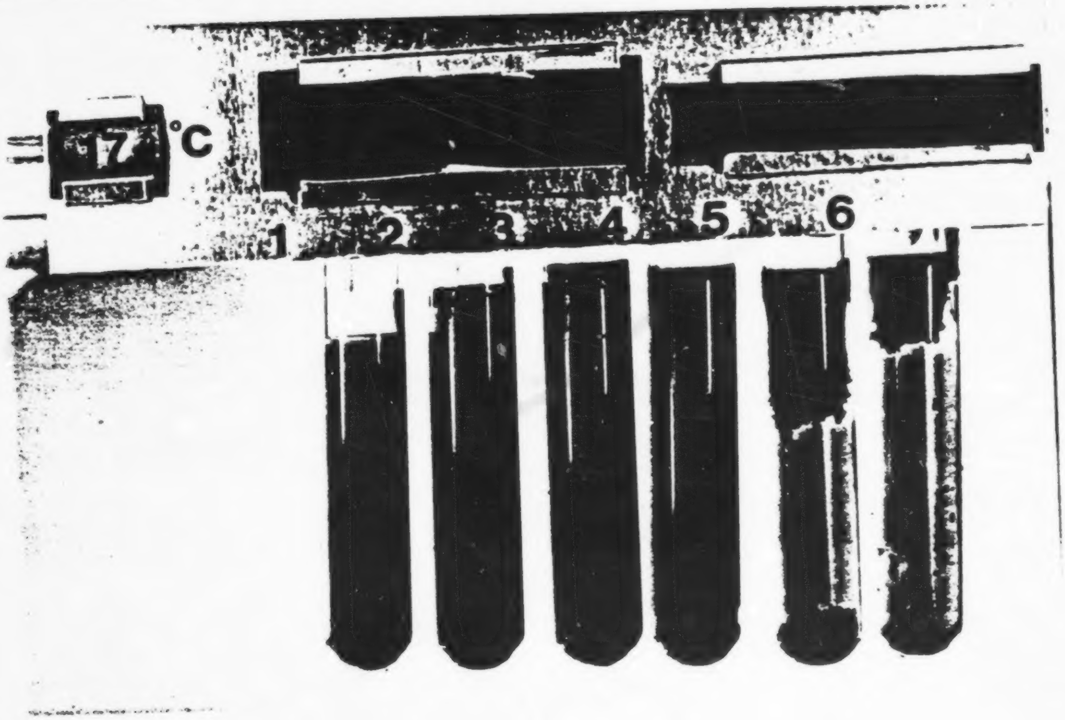

17 °C
1
2
3
4
5
6
17 °C
1
2
3
4
5
6

Figure 18: Temperature effect, BC-47, 17°C reaction temperature


17 °C
1
2
3
4
5
6
7


17 °C
1
2
3
4
5
6
7

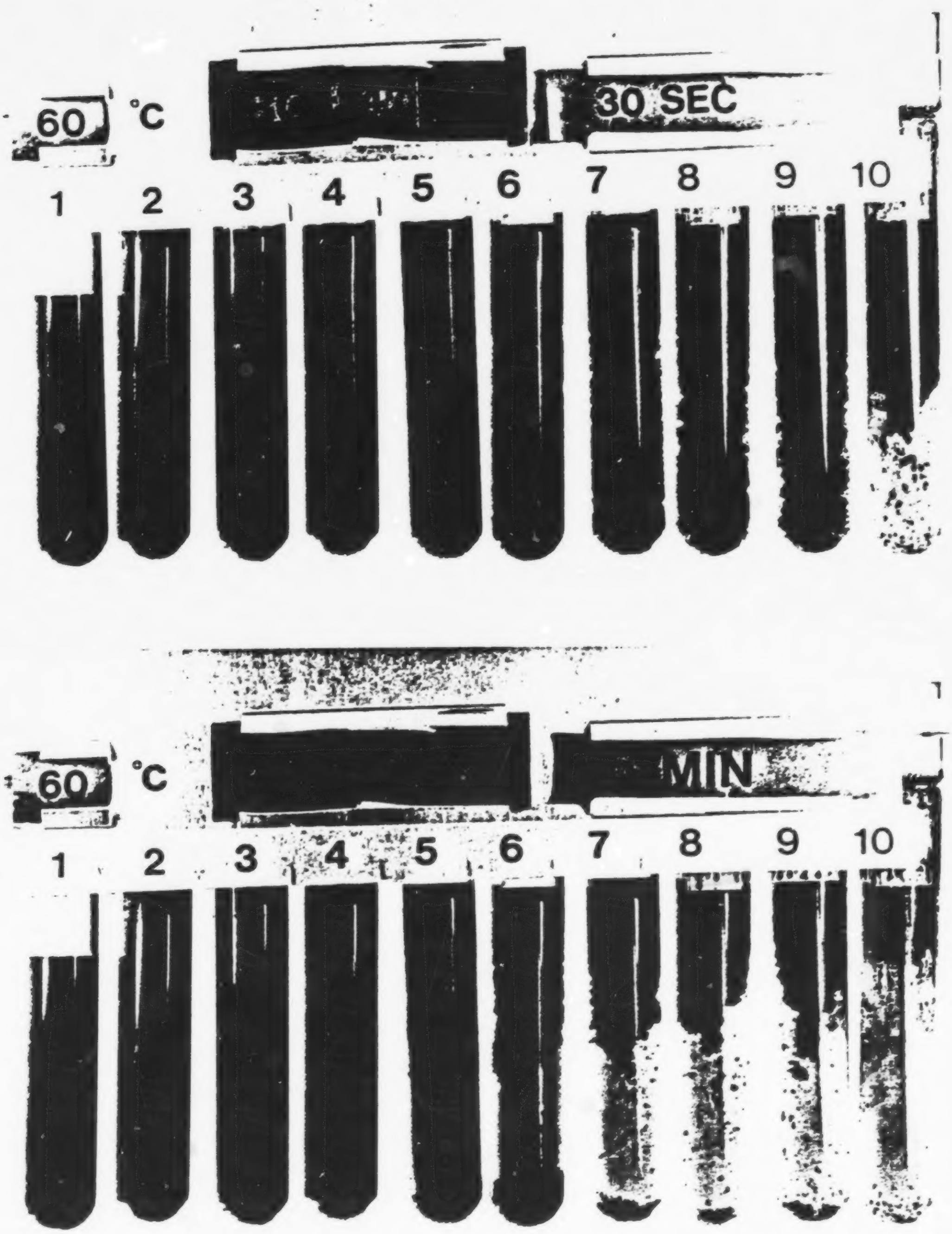
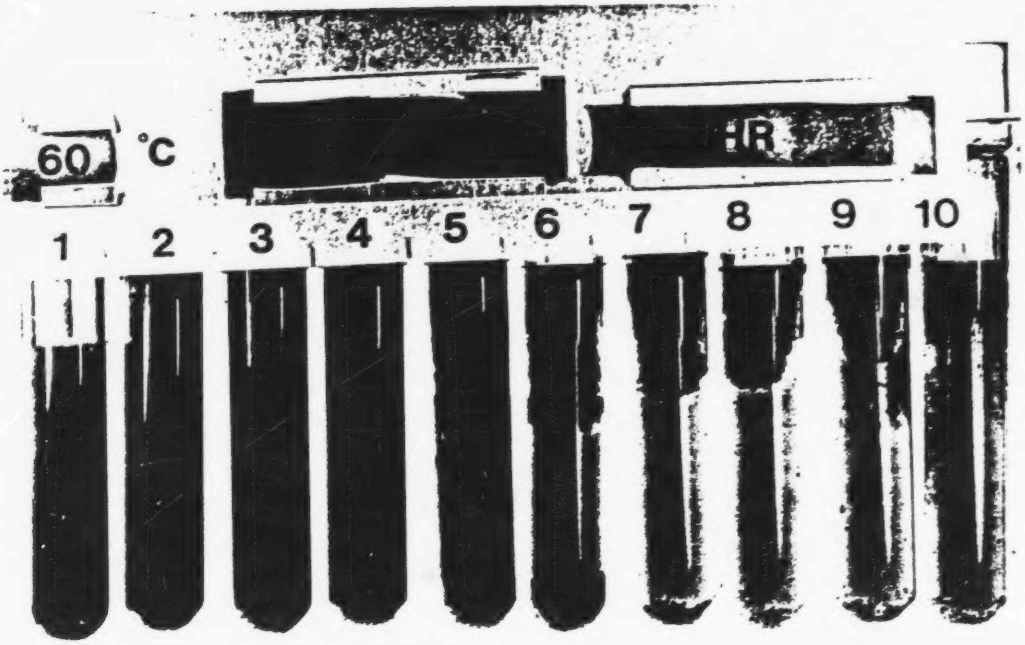
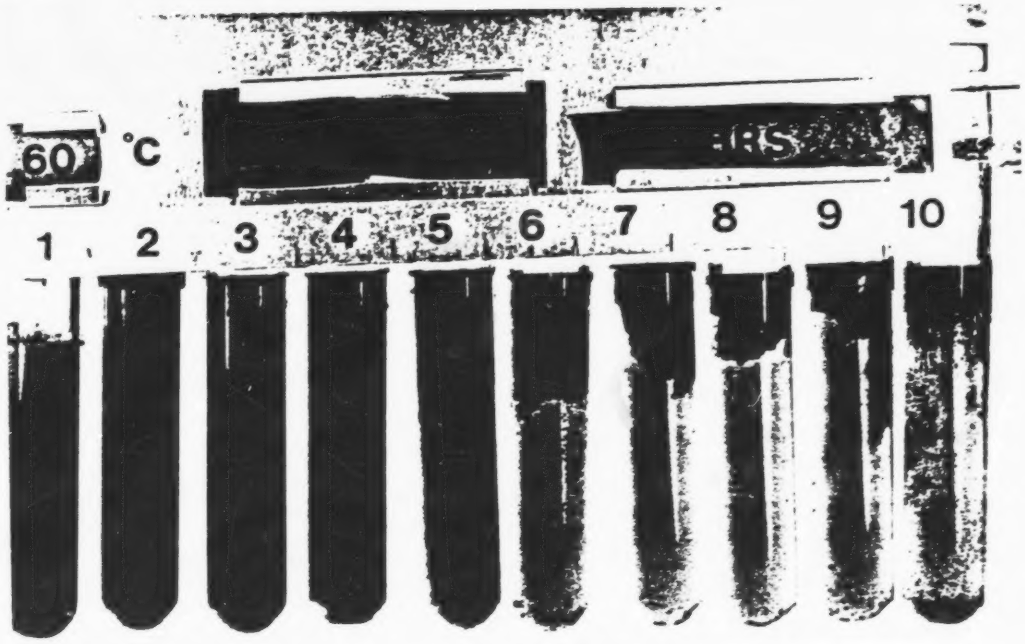

60 °C
30 SEC
1 2 3 4 5 6 7 8 9 10
60 °C
MIN
1 2 3 4 5 6 7 8 9 10

Figure 19: Concentration optimization, BC-47
#1=emulsion only, #2=emulsion+toluene+water, #3=90ppm, #4=100ppm, #5=110ppm, #6=120ppm, #7=150ppm, #8=175ppm, #9=200ppm, #10=400ppm


60 °C
HR
1
2
3
4
5
6
7
8
9
10


60 °C
HRS
1
2
3
4
5
6
7
8
9
10

COULTER COUNTER Model T & TA PARTICLE SIZE ANALYSIS

ORGANIZATION

OPERATOR

EQUIPMENT

SAMPLE ELECTROLYTE DISPERSANT

Figure 20: Initial analysis of stock emulsion

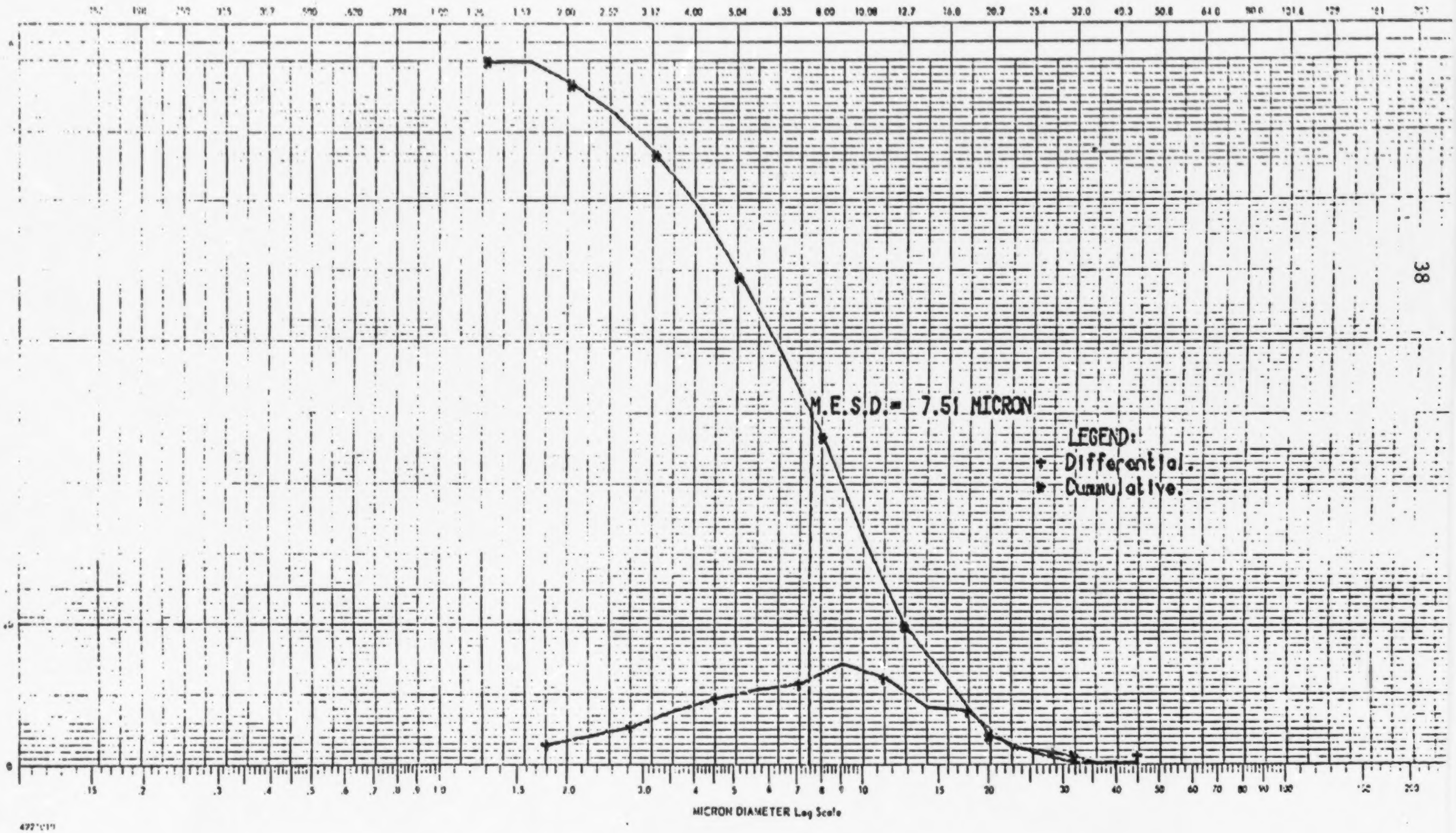
$k = d\sqrt[3]{2w}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1 FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1 FOR MODEL TA

SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	± IA	A	DIA.	W	± IA	A

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



COULTER COUNTER Model T&TA

PARTICLE SIZE ANALYSIS

.15 – 200 μ
% PERCENT

COULTER ELECTRONICS INC
590 W 20 ST.
HIALEAH FLA. 33010

ORGANIZATION

OPERATOR

EQUIPMENT

SAMPLE ELECTROLYTE DISPERSANT

Figure 21: BC-44, 400ppm

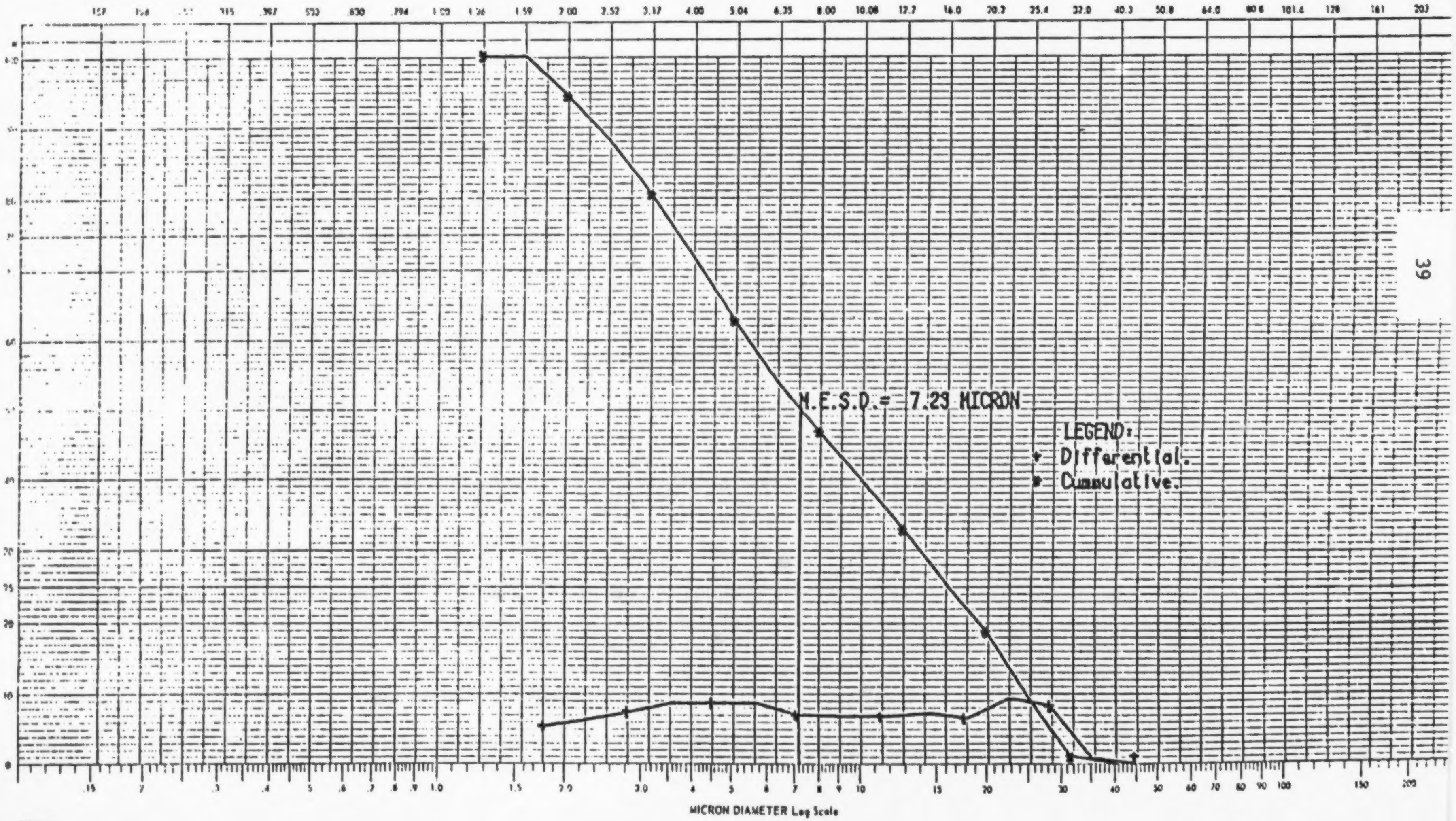
$k = d\sqrt[3]{2^w}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1
FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1
FOR MODEL TA

APER. SIZE	SERIAL		PART DIA.	W	± IA	A	DIA.	W	± IA	A

SAMPLE SETTINGS

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



COULTER COUNTER Model T & TA

PARTICLE SIZE ANALYSIS

.15 – 200 μ
X PERCENT

ELECTRONICS INC.
590 W 20 ST.
HIALEAH, FLA. 33010

$k = d\sqrt[3]{2w}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when $W2 = W1$
FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when $W2 = W1$
FOR MODEL TA

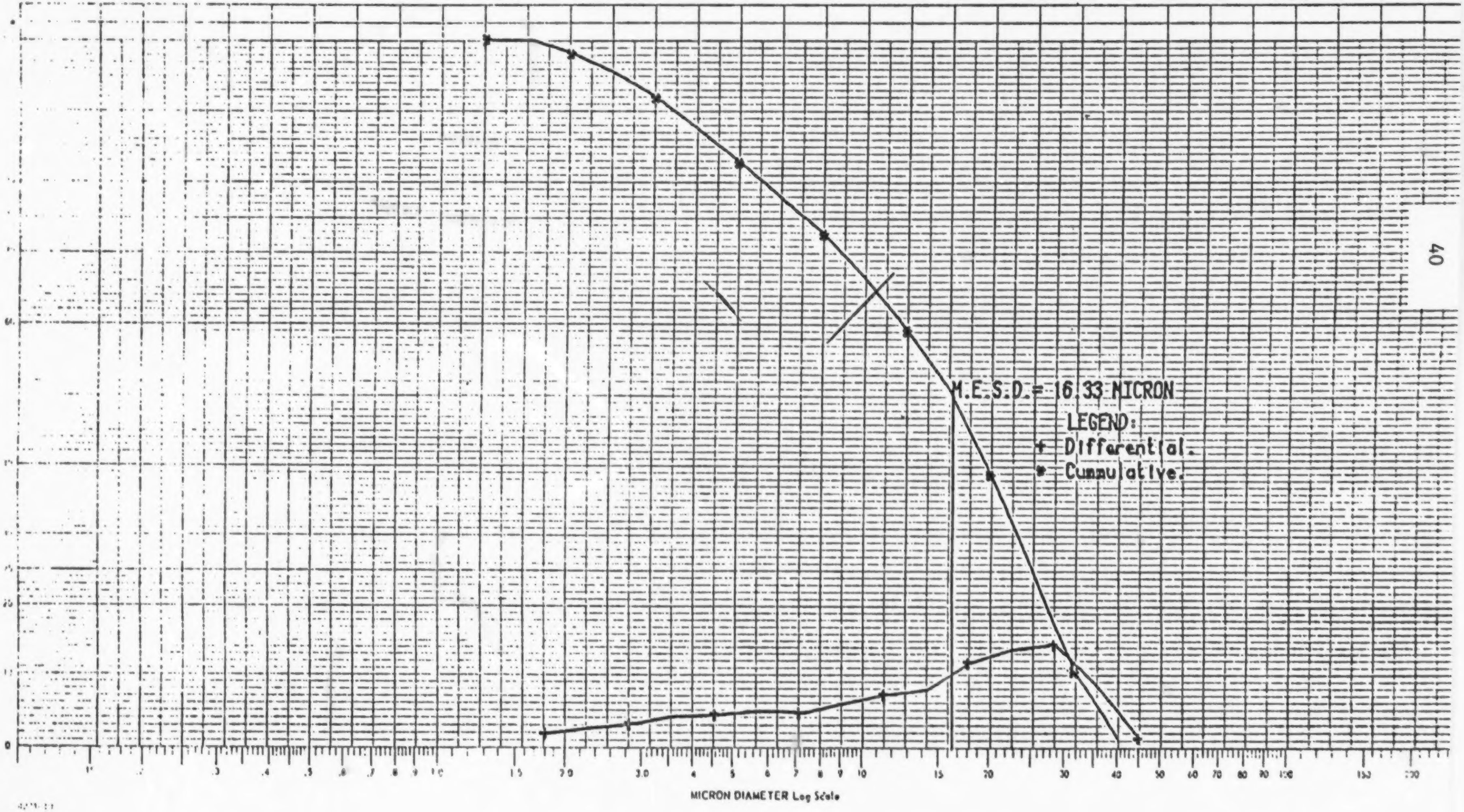
SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	± IA	A	DIA.	W	± IA	A

SAMPLE ELECTROLYTE DISPERSANT

Figure 22: BC-46, 200ppm

SIZE DISTRIBUTION PLOT BY 180 MICRON APERTURE TUBE.



COULTER COUNTER Model T & TA

PARTICLE SIZE ANALYSIS

.15 - 200μ
X PERCENT

ER ELECTRONICS INC.
590 W 20 ST.
HIALEAH FLA. 33010

OPERATOR

SAMPLE

ELECTROLYTE

DISPENSANT

$k = d\sqrt[3]{2w}$

$\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when $W2 = W1$

FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when $W2 = W1$

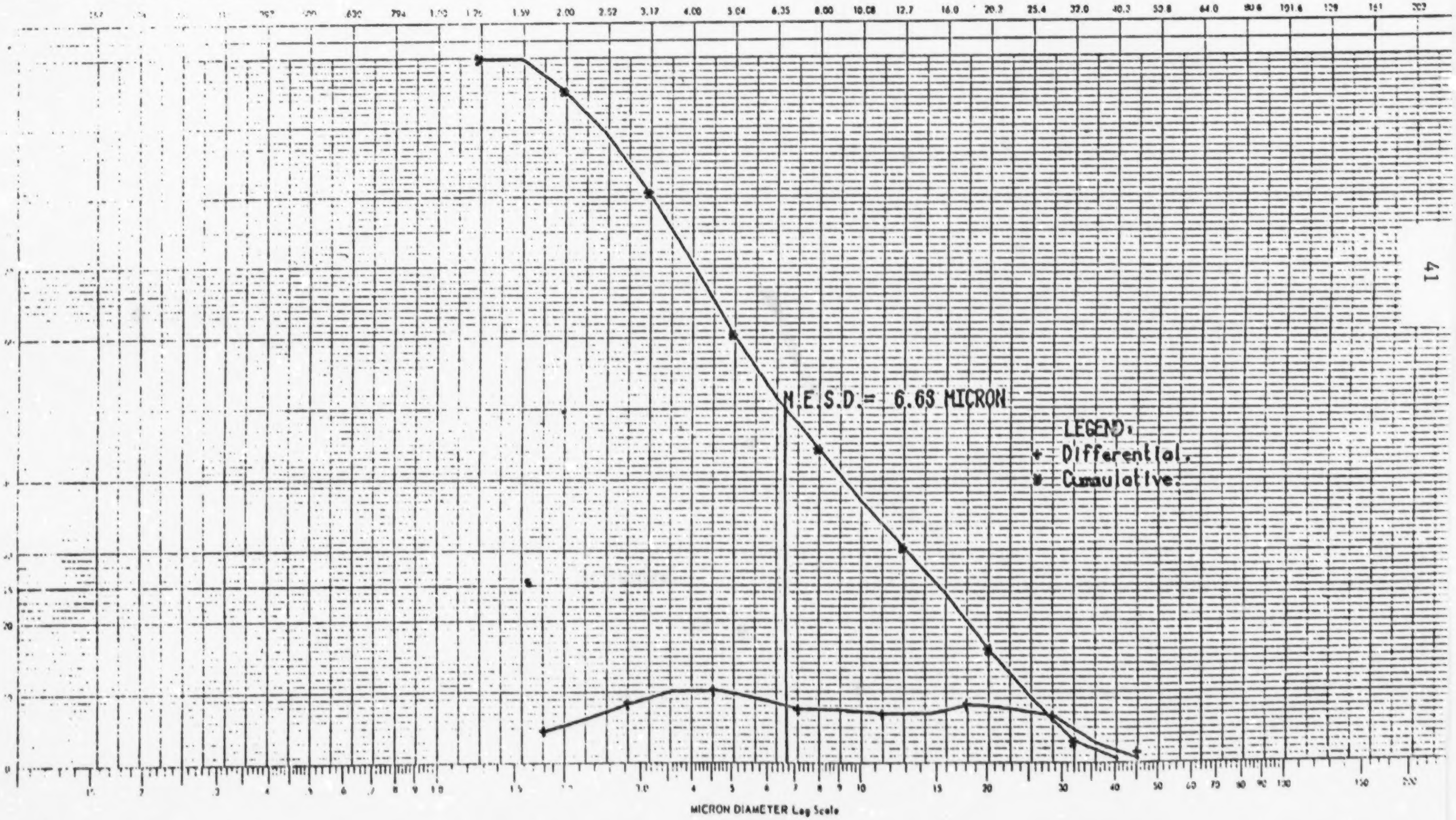
FOR MODEL TA

SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	± ΔA	A	DIA.	W	± ΔA	A

Figure 23: BC-46, 400ppm

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



COULTER COUNTER® Model T & TA   PARTICLE SIZE ANALYSIS

$k = d\sqrt[3]{2^w}$ $\frac{A_2}{A_1} = \left(\frac{d_2}{d_1}\right)^3$ when W2 = W1 $\frac{A_2}{A_1} = \left(\frac{d_1}{d_2}\right)^3$ when W2 = W1

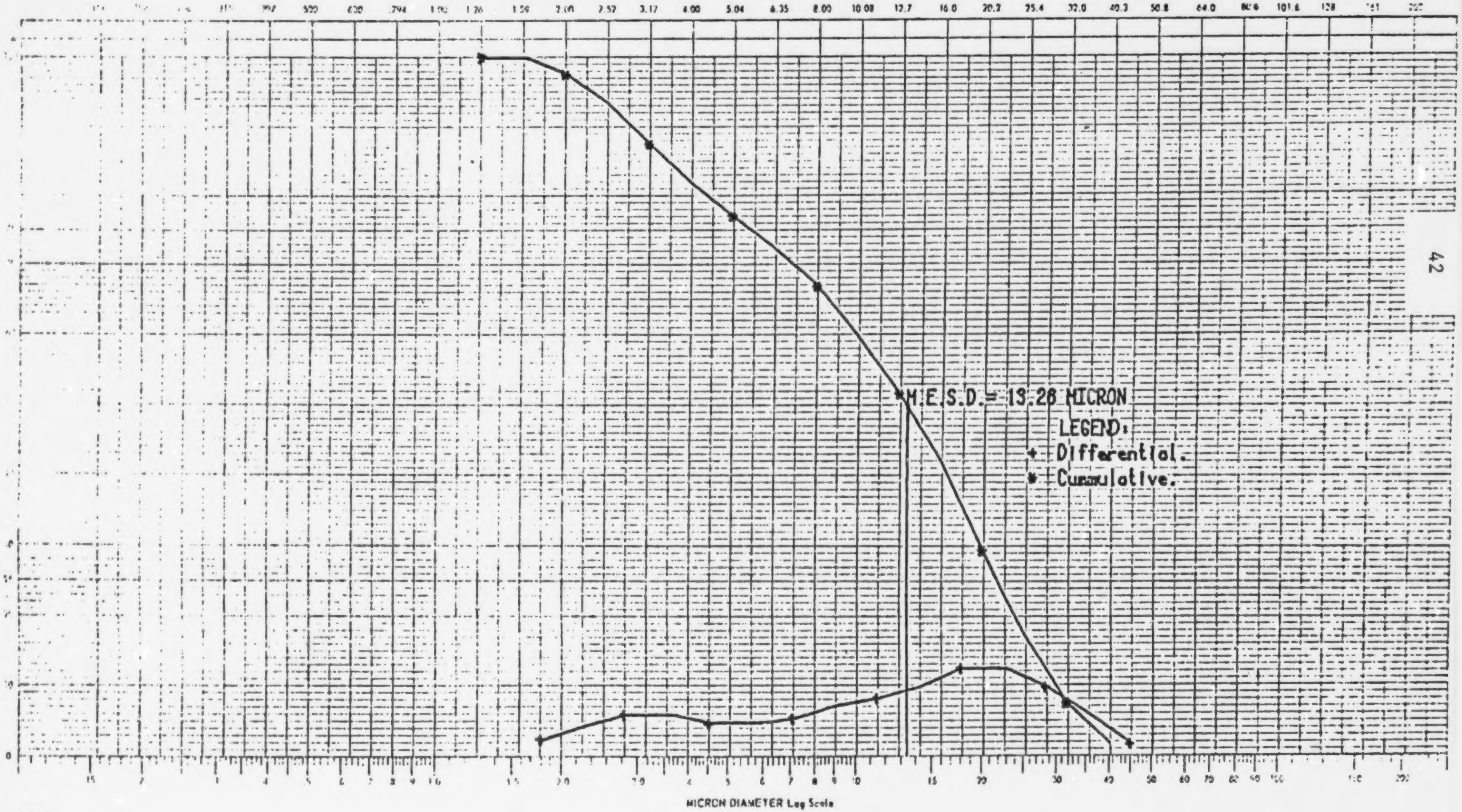
FOR MODEL T   FOR MODEL TA   SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	1/A	A	DIA.	W	1/A	A

ELECTROLYTE   DISPERSANT

Figure 24: BC-47, 100ppm

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



Model TaTA

PARTICLE SIZE ANALYSIS

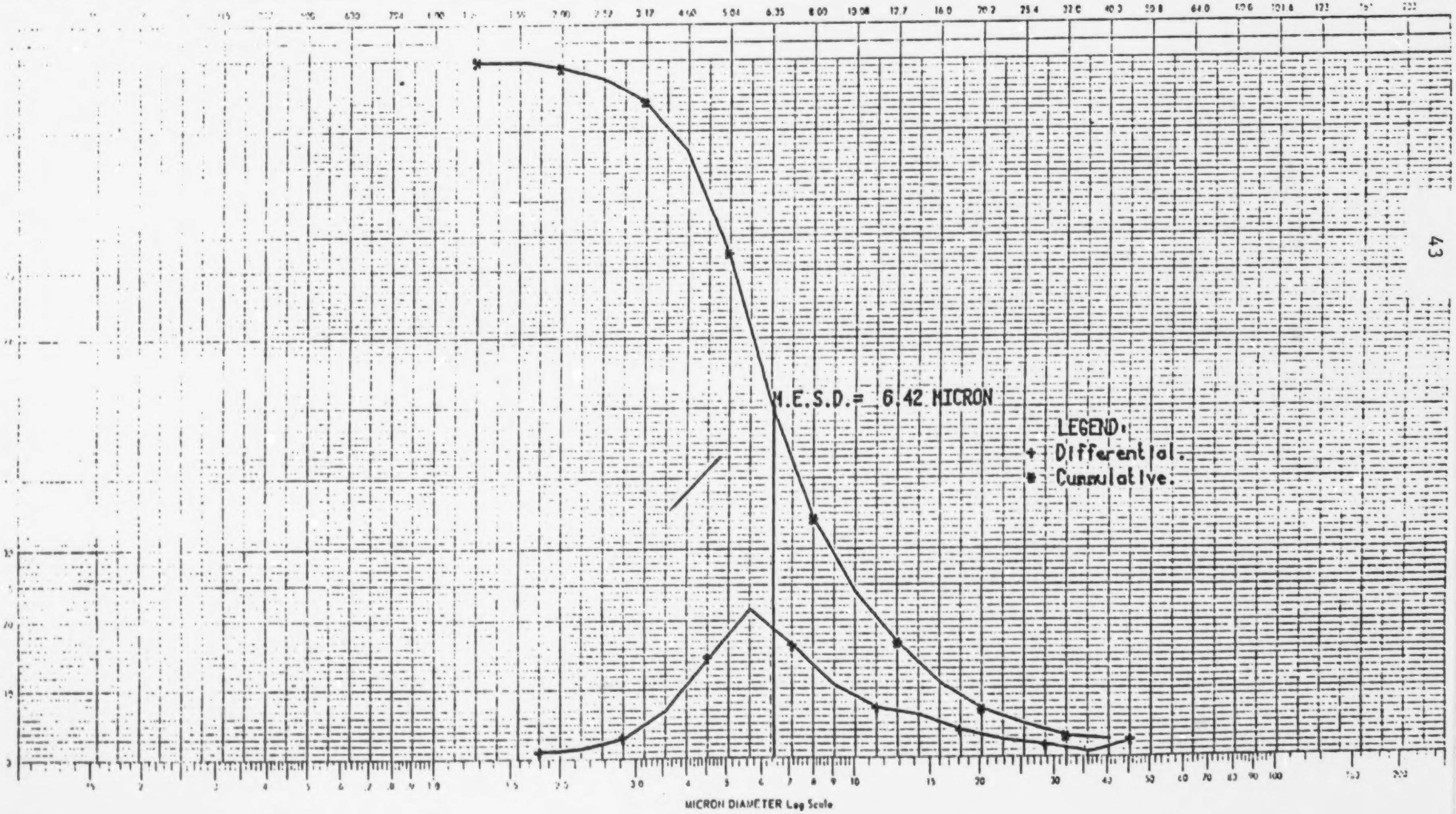
$b = d\sqrt[3]{\overline{2w}}$ FOR MODEL T		$\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1	$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1 FOR MODEL TA				SAMPLE SETTINGS			
APER. SIZE	SERIAL		PART DIA.	W	± IA	A	DIA.	W	± IA	A

ELECTROLYTE

DISPERSANT

Figure 25: BC-47, 200ppm

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



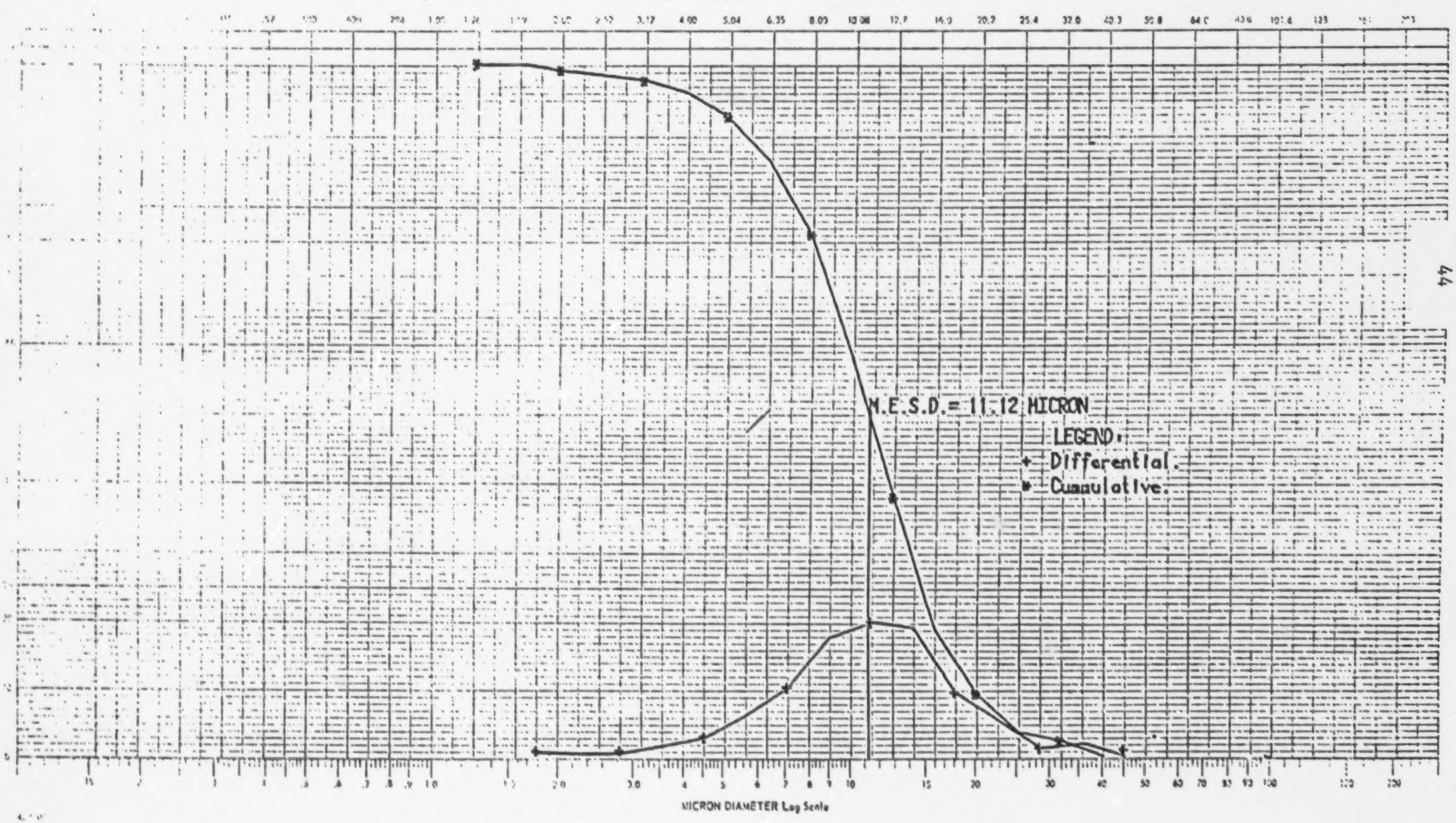
COULTER COUNTER Model T&TA PARTICLE SIZE ANALYSIS

OPERATOR

ELECTROLYTE DISPERSANT

$k = d\sqrt[3]{2^w}$		$\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1	$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1				SAMPLE SETTINGS			
FOR MODEL T			FOR MODEL TA							
APER. SIZE	SERIAL		PART DIA.	W	±TA	A	DIA.	W	±TA	A

Figure 26: BC-47, 400ppm



SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.

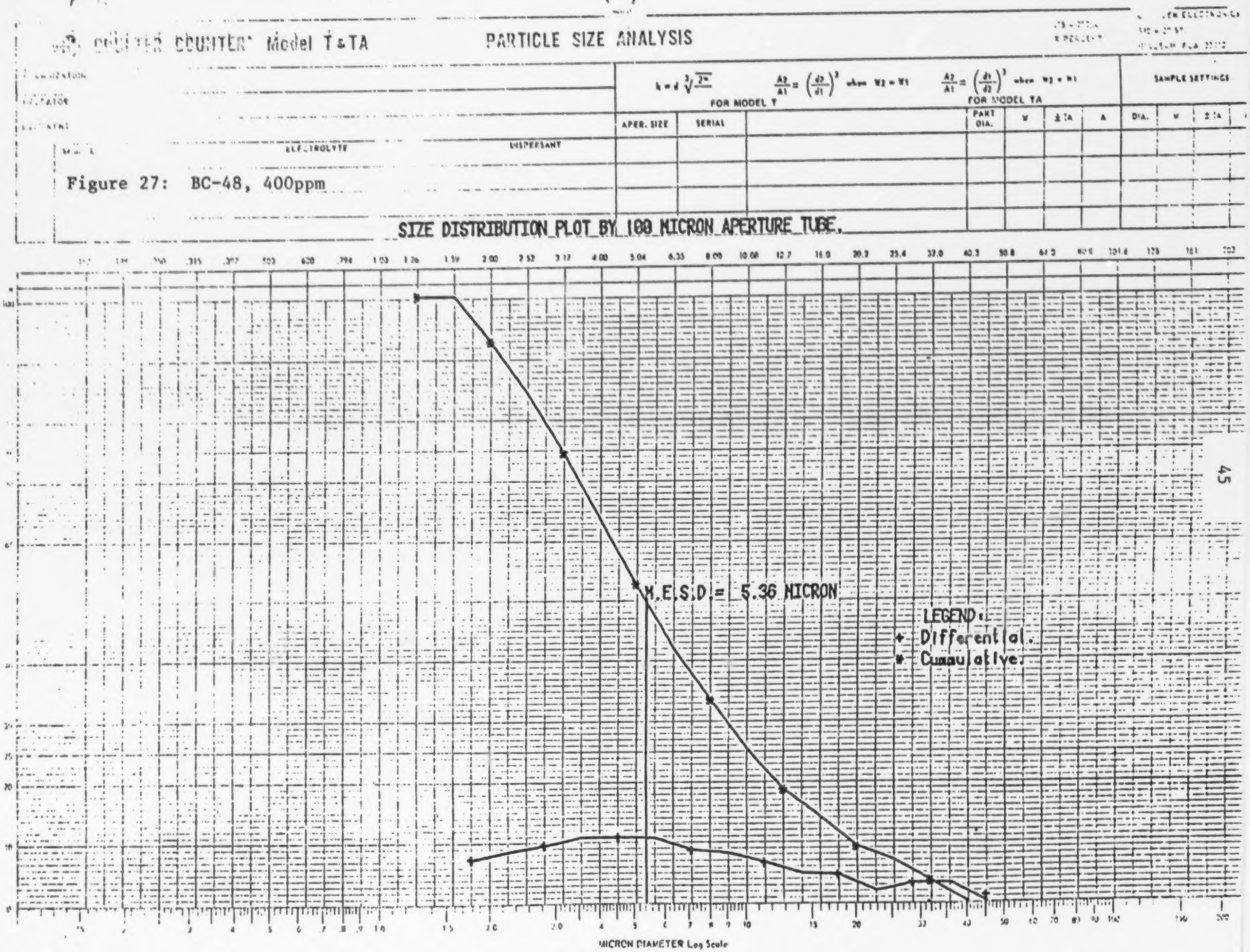


Figure 27: BC-48, 400ppm

COULTER COUNTER Model T & TA

PARTICLE SIZE ANALYSIS

% PERCENT

HALEAH FLA. 33010

$k = d\sqrt[3]{2w}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when $W2 = W1$ FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when $W2 = W1$ FOR MODEL TA

SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	± 1/A	A	DIA.	W	± 1/A	A

OPERATOR

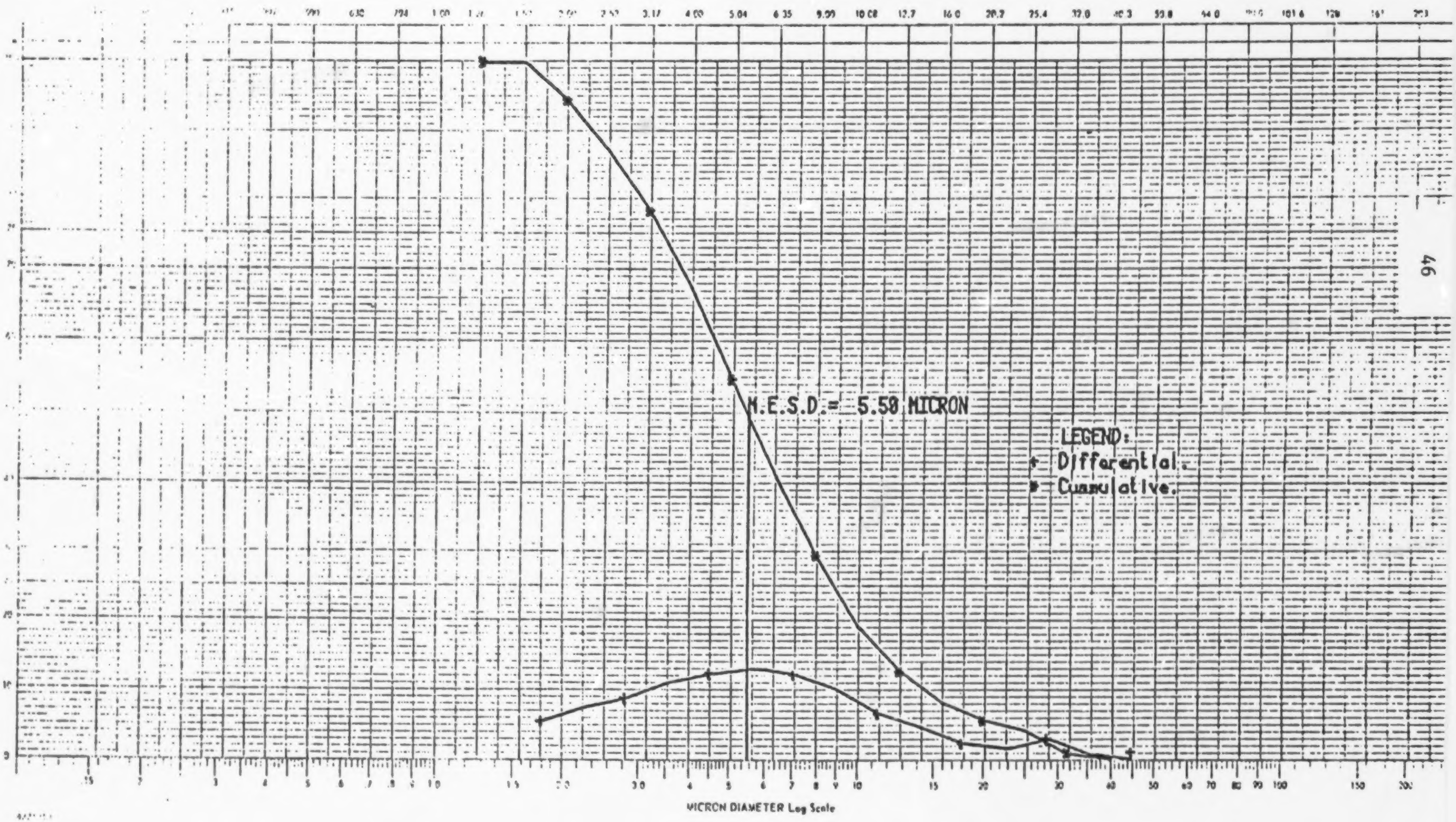
SAMPLE

ELECTROLYTE

DISPERSANT

Figure 28: BC-50, 200ppm

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



COULTER COUNTER Model T & TA

PARTICLE SIZE ANALYSIS

.15 – 200 μ
X PERCENT

OPERATOR

ELECTROLYTE

DISPERSANT

Figure 29: BC-50, 400ppm

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.

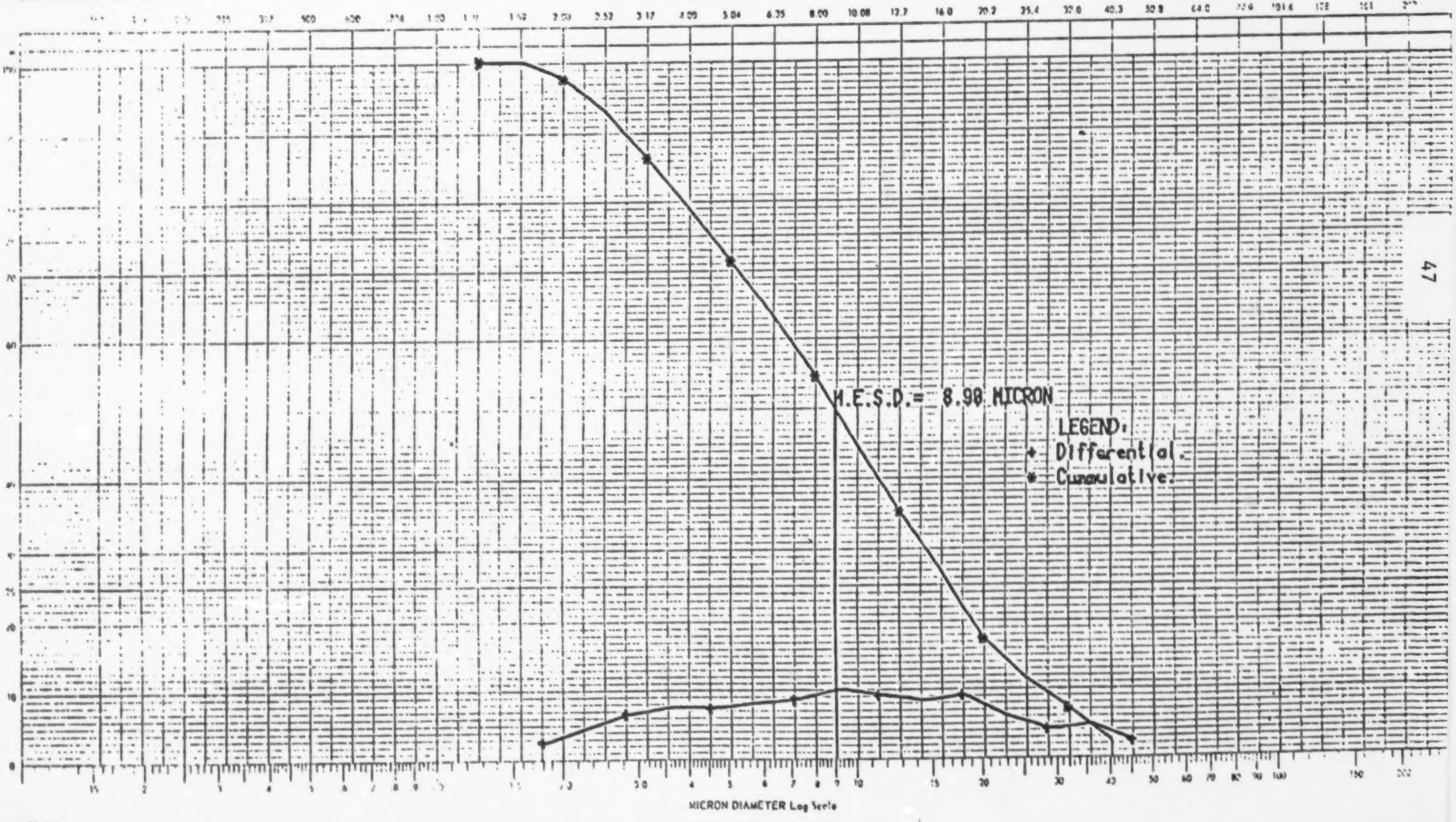
$k = d\sqrt[3]{2^w}$ FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1 $\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 ≠ W1 FOR MODEL TA

APER. SIZE	SERIAL		PART DIA.	W	± IA	A

SAMPLE SETTINGS

DIA.	W	± IA	A



COULTER COUNTER® Model T&TA PARTICLE SIZE ANALYSIS

.15 – 200μ
% PERCENT

COULTER ELECTRONICS INC.

OPERATOR

EQUIPMENT

ELECTROLYTE

DISPERSANT

Figure 30: BC-17, 100ppm

$k = d\sqrt[3]{2^w}$

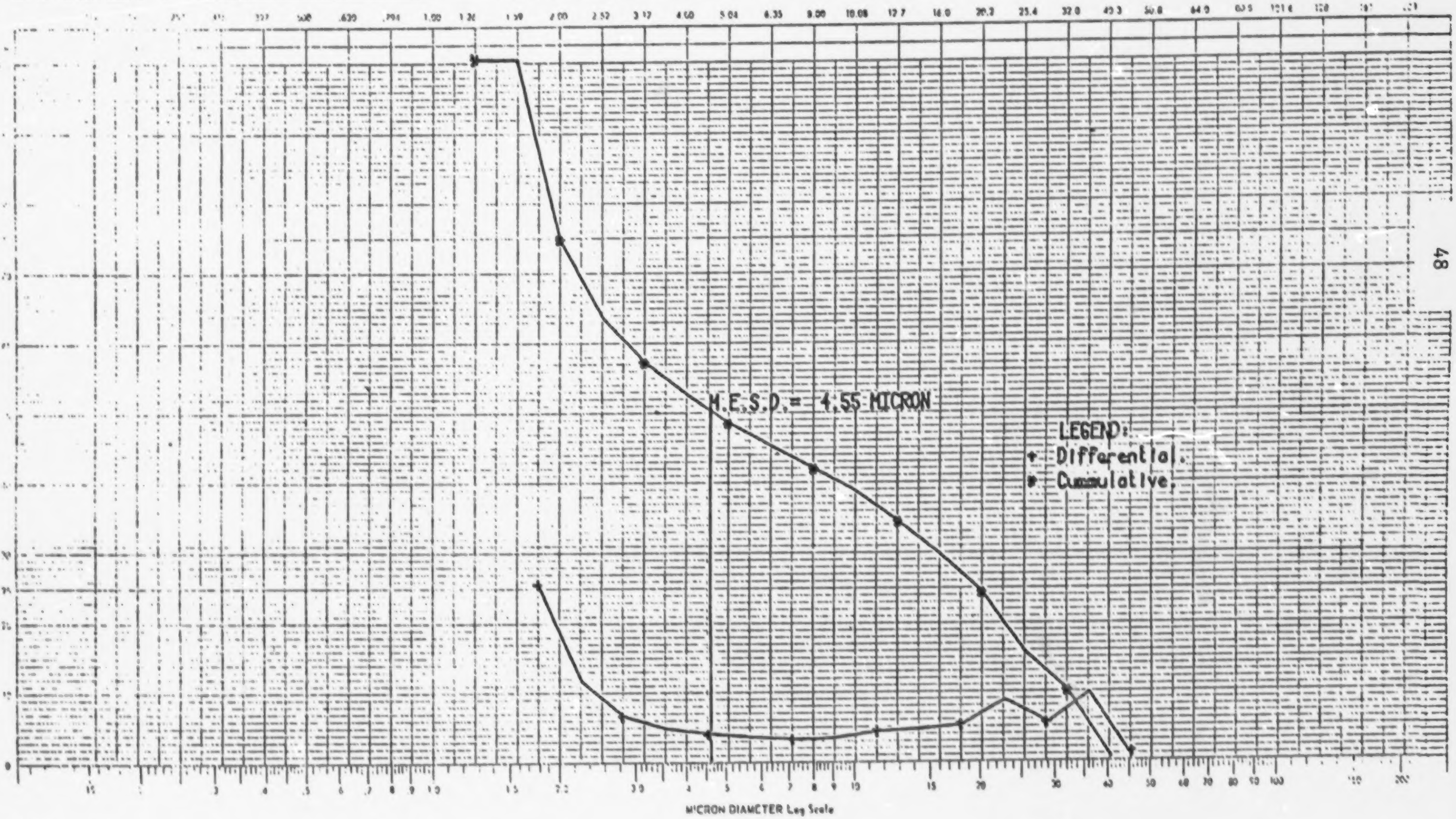
FOR MODEL T: $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1

FOR MODEL TA: $\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1

SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	±IA	A	DIA.	W	±IA	A

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.



COULTER COUNTER® Model T&TA

PARTICLE SIZE ANALYSIS

% PERCENT

OPERATOR

EQUIPMENT

SAMPLE

ELECTROLYTE

DISPERSANT

Figure 31: BC-17, 200ppm

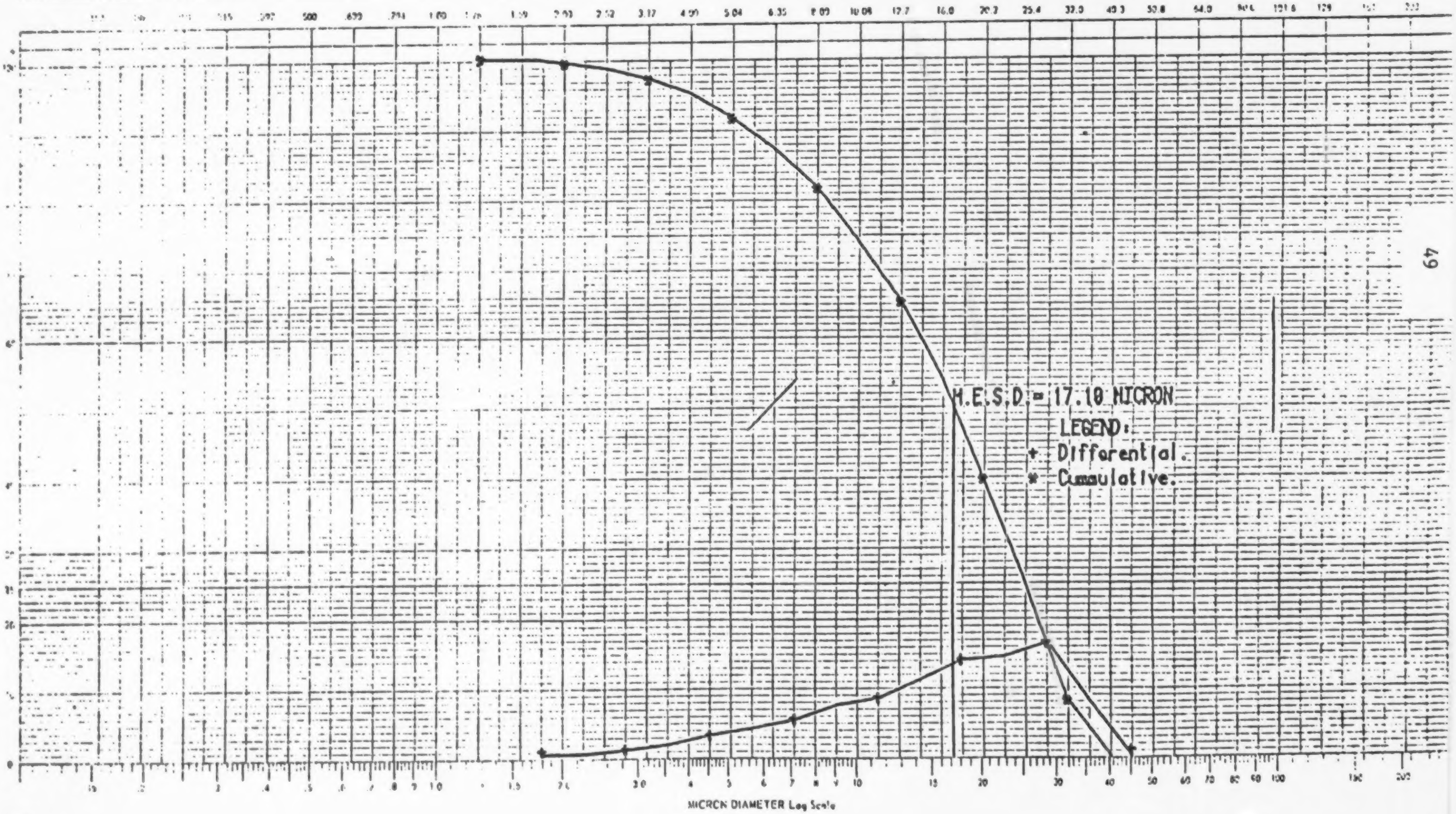
$h = d\sqrt[3]{2^w}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1 FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1 FOR MODEL TA

SAMPLE SETTINGS

APER. SIZE	SERIAL		PART DIA.	W	± TA	A	DIA.	W	± TA	A

SIZE DISTRIBUTION PLOT BY 100 MICRON APERTURE TUBE.

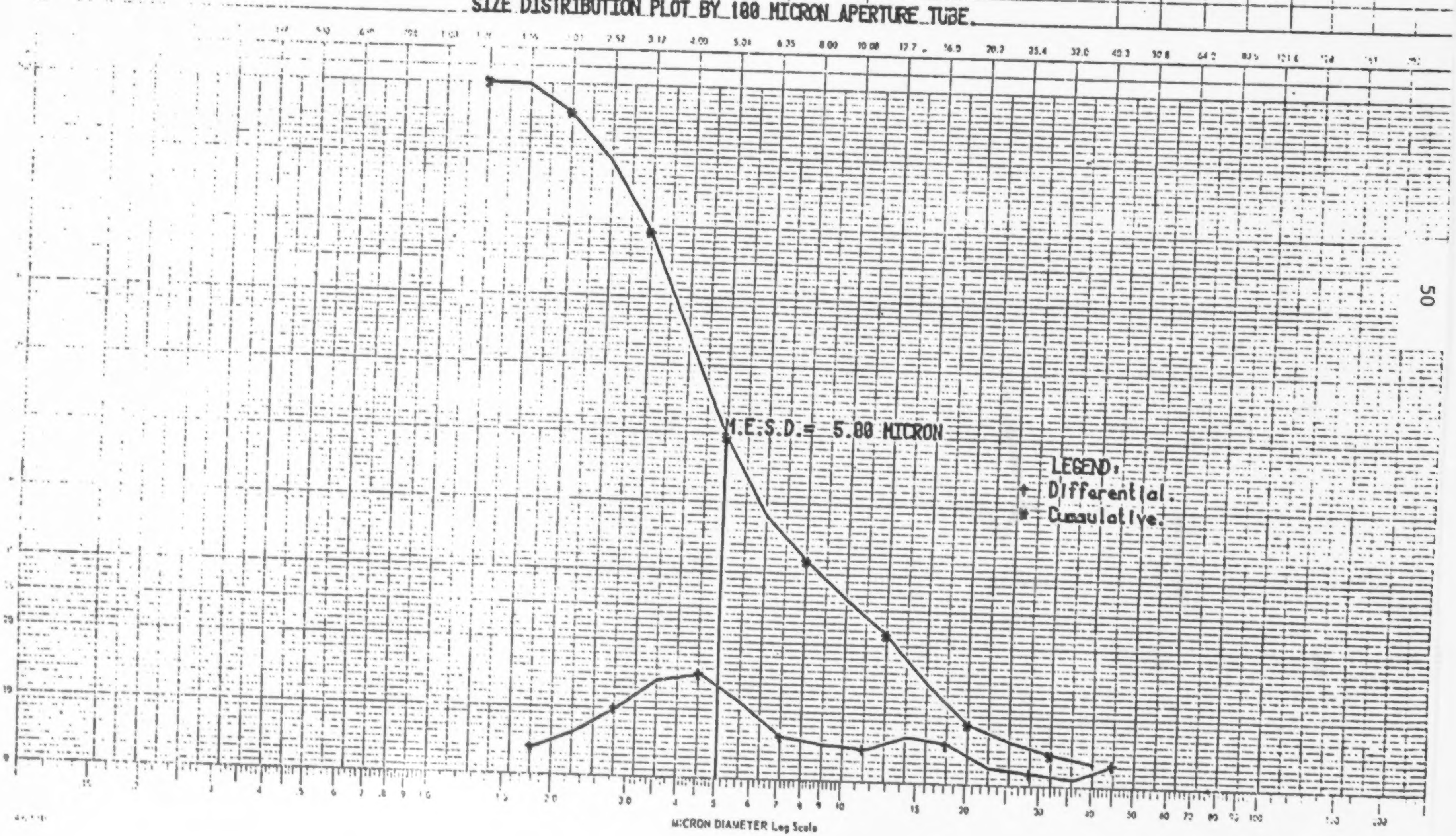


COULTER COUNTER Model T & TA

PARTICLE SIZE ANALYSIS

		$k = d\sqrt[3]{2w}$ FOR MODEL T	$\frac{A_2}{A_1} = \left(\frac{d_2}{d_1}\right)^3$ when $W_2 = W_1$		$\frac{A_2}{A_1} = \left(\frac{d_1}{d_2}\right)^3$ when $W_2 = W_1$ FOR MODEL TA				SAMPLE SETTINGS			
SAMPLE	ELECTROLYTE	DISPERSANT	APER. SIZE	SERIAL	PART DIA.	W	± ΣA	A	DIA.	W	± ΣA	A

Figure 32: BC-17, 400ppm



APPENDIX A ANALYTICAL PROCEDURES

A. MOISTURE DETERMINATION

Principle

The Mitsubishi Moisture Meter model CA-02 combines coulometry with the Karl Fischer titration method. Water is titrated by the electrolytic generation of a Karl Fischer reagent which reacts with water as follows:

$$I_2 + SO_2 + 3C_5H_5N + H_2O \rightarrow 2C_5H_5N.HI + C_5H_5N.SO_3 \qquad (1)$$

$$C_5H_5N.SO_3 + CH_3OH \rightarrow C_5H_5N.HSO_4CH_3 \qquad (2)$$

In this Coulometry-Karl Fischer titration, the sample is added to a pyridine-methanol solution (with iodide ion and sulphur dioxide as principal components). Iodine, generated electrolytically at the anode, reacts with the water in the sample as shown in equations (1) and (2). Iodine is generated in direct proportion to the quantity of electricity according to Faraday's Law. For example:

$$2I^- - 2e^- \rightarrow I_2 \qquad (3)$$

One mole of iodine reacts quantitatively with one mole of water. Therefore, 1 mg of water is equivalent to 10.71 coulombs. Based on this principle, water content is directly determined from the quantity of electricity (coulombs) required for electrolysis.

Sample Preparation and Procedure

The samples to be analyzed are sufficiently diluted with tetrahydrofuran so that the final concentration for water is within the range of 10 μg to 20 mg H_2O, per injection. The diluted sample is drawn into a preweighed syringe and the sample and syringe are weighed. A known volume of sample is then injected into the titration vessel. The weight of sample injected is then determined by weighing the empty syringe. The digital readout gives the micrograms of water contained in the injected sample. By applying dilution factors and subtracting the amount of water contained in a THF blank, the percentage of water in the sample can be calculated as follows:

$$\%H_2O = \frac{(H_2O \text{ in sample} - H_2O \text{ in blank})\ (\mu g) \times \text{dilution factor (s)} \times 10^{-4}}{\text{wt injected sample (g)}}$$

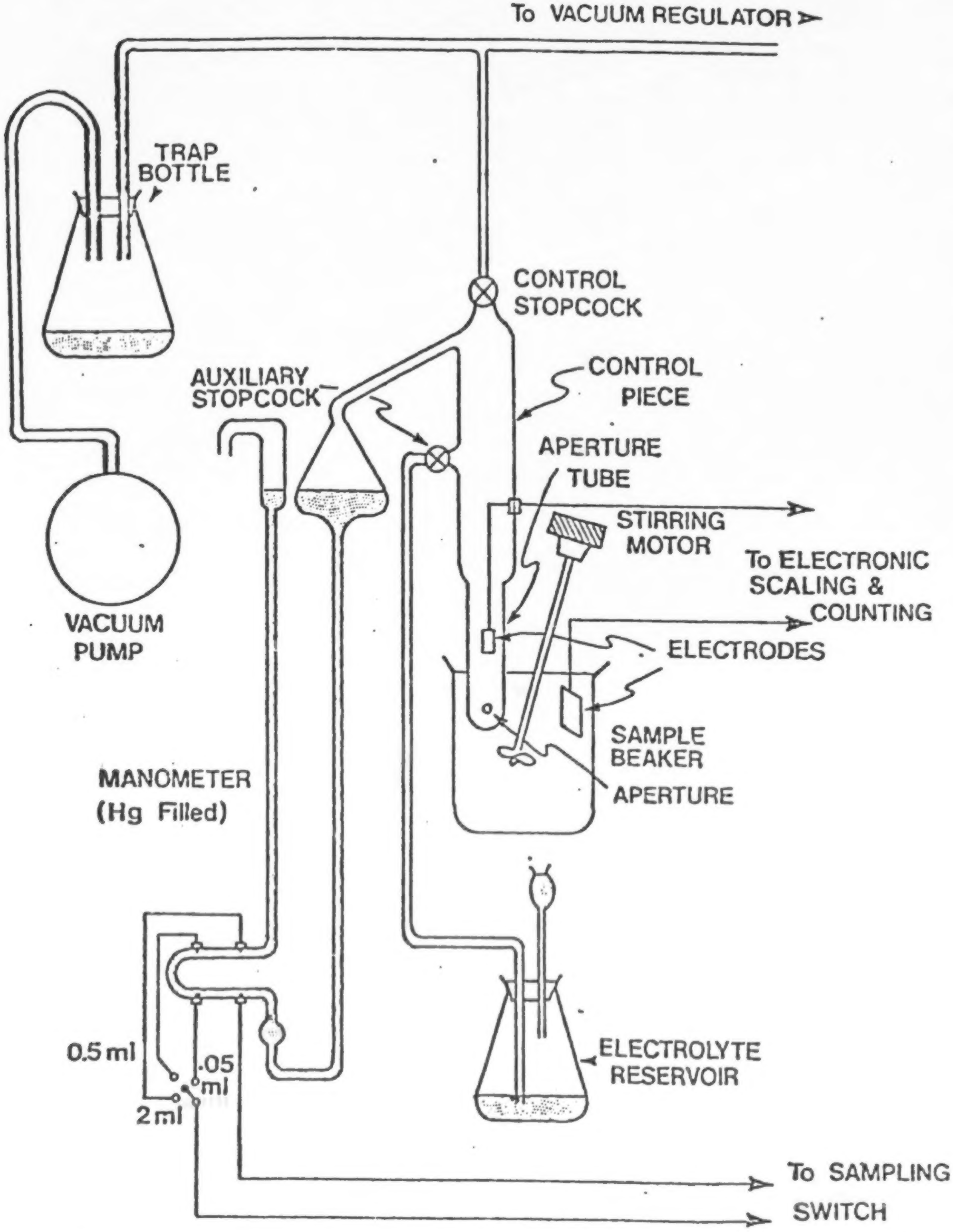
B. COUTER COUNTER ANALYSIS

Principle

The principle of operation, referred to as the Coulter principle or the electronic sensing zone method, may be summarized as follows (see attached schematic).

The particles to be analyzed are suspended in a conductive liquid (electrolyte) and the suspension is forced by vacuum to flow through a small aperture in a glass tube. Electrodes are immersed in the conducting liquid on opposite sides of the aperture and a current passed between them. As the current must pass through the aperture, the concurrent passage of a particle will change the resistance between the electrodes. This produces a current pulse of short duration whose magnitude is, within limits, proportional to the particle volume. Current change pulses resulting from the passage of particles through the aperture are electronically converted into voltage pulses, which are amplified and then sized into 16 discrete channels by means of threshold circuits. Cumulative as well as differential volume data may be obtained. The number of pulses (particles) in each size range (channel) is also recorded. All data may be obtained via a numeric readout or tape printer.

Apertures are available in sizes ranging from 15μm to 2000μm. The useful range of an aperture tube is from approximately 2% to 40% of the aperture diameter. The current change induced by the passage of particles


To VACUUM REGULATOR
TRAP BOTTLE
CONTROL STOPCOCK
CONTROL PIECE
AUXILIARY STOPCOCK
APERTURE TUBE
STIRRING MOTOR
To ELECTRONIC SCALING & COUNTING
VACUUM PUMP
ELECTRODES
SAMPLE BEAKER
APERTURE
MANOMETER (Hg Filled)
0.5 ml
.05 ml
2 ml
ELECTROLYTE RESERVOIR
To SAMPLING SWITCH

The Coulter Counter: A Schematic of the Particle Sensing System.

with diameters less than 2% of the aperture diameter becomes too small to be reliably detected and may be masked by electronic noise and interference effects. The response of the instrument to particles larger than 40% of the aperture diameter begins to significantly deviate from linearity; i.e., the response is no longer proportional to particle volume.

Each aperture tube is calibrated using standards of known size. Synthetic polymer latex particles, which are spherical, low-density, non-porous and essentially mono-sized are most frequently used.

The conducting liquid (electrolyte) must be chosen to meet the conductivity requirements of the aperture and should not react in any way with the particulate system to be analysed. The current flow through the aperture is adjustable; the optimum value depends on the size of the aperture and the conductivity of the electrolyte used. Proper aperture current is necessary to obtain maximum signal to noise ratio during operation. In our laboratory, noise generated as a result of external interferences was minimized by construction of a Faraday cage around the sample stand.

As previously stated the Coulter Counter sizes each pulse (particle) into one of sixteen channels; the assignment of particle size to channel being accomplished by electronic thresholds built into the instrument. A regular geometric size progression exists throughout the sixteen channels. Each channel accumlates particles within 2:1 volumetric size range or a diameter range of $\sqrt[3]{2}$. A three-channel span therefore represents a diameter change of 2:1. The amount of sample analyzed is determined by presetting (1) the time (duration) of the count, (2) the number of particles to be counted, or (3) the volume of sample on which the accumulation is to be made. Sufficient data should be obtained to allow the instrument to normalize the size distribution to 100%. Time required for one accumulation is 1-2 min; normally three accumulations are made and the average taken.

Differential and cumulative volume per cent data for each channel (size range) are typically plotted. Median particle (droplet) size known as MESD (Median Equivalent Spherical Diameter) is conveniently taken as the 50%

point on the cumulative curve.

Sample Preparation and Procedure

The samples measured with the Coulter counter are mostly aqueous and the particulates to be measured (whether as solids or oil) are the minor component. These samples must be pre-filtered to remove materials too large for the size of aperture in use. For example, when using a 100 μm aperture, the samples are pre-filtered through a 400 mesh (38 μm) screen because the maximum particle size that should be present is 40 μm. When required, the dry weight of this "coarse" material if significant, can be added to the results obtained from the Coulter Counter if, for example, the % oil in a water layer is being determined.

Once the sample is properly screened it is sufficiently diluted in an aqueous electrolyte solution such that the particulates can pass through the sensing zone (aperture) one at a time. An electrolyte solution marketed by Coulter under the trade name "Isoton" is used, the composition of which is given below:

Sodium chloride	7.93 g/l
Disodium EDTA	0.38 g/l
Potassium chloride	0.40 g/l
Monosodium phosphate	0.19 g/l
Disodium phosphate	1.95 g/l
Sodium fluoride	0.50 g/l

The diluted sample is then added to more electrolyte such that the concentration of particulates is sufficient for analysis. This solution is then drawn through the aperture to obtain % volume and count data for each channel. Having these data plus the dilution factors and knowing the volume of sample analyzed (drawn through the aperture) allows calculation of % particulates in the original sample and the plotting of a size distribution graph. A computer program is used to simplify the calculations.

The size of oil particles present in the fluid sample to be analyzed should fall within the useful range of a single aperture tube. In cases where the size distribution is not within this range there may be a loss of fine particles below the lower limit or a loss of coarser particles above the higher limit.Therefore smaller, or larger aperture tubes, respectively, will be required.

C. TOTAL OIL ANALYSIS

This determination was done to provide a reliable value for the percent total oil or bitumen contained in the emulsion used for the demulsifier testing. It was apparent that during the screening (400 mesh, 38 microns) of the emulsion prior to its analysis by Coulter Counter, that there was some material coarser than 38 microns left on the screen and that some method of including this material in the % total oil value had to be used.

This was achieved by placing a sample of the emulsion in an oven and evaporating off the water. Thus, 25ml of the emulsion was added to a tared beaker and the weight of the emulsion recorded. The beaker was then placed in an oven at 110°C overnight (approximately 16 hours). Further heating showed negligible weight loss. After cooling and weighing the residue, which was assumed to be all bitumen, the percent oil can be calculated.

This method is not totally accurate since some of the more volatile hydrocarbons may also be lost or alternatively, not all of the water may have been driven off. However, the value obtained for percent total oil is thought to be a reasonable approximation of that actually contained in the emulsion.